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AUTHORITY

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Report No. IITRI-U6044-11

INVESTIGATION OF CHEMICAL SPECIES
AND TEMPERATURES PRESENT IN PYROTECHNIC FLAMES

Final Technical Report

by

E. L. Grove
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DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Weapons Development and Engineering Laboratories
Ground Munitions Laboratory
Edgewood Arsenal, Maryland 21010

Contract No. DA-18-035-AMC-739(A)

IIT RESEARCH INSTITUTE
10 West 35th Street
Chicago, Illinois 60616

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Contract No. DA-18-035-AMC-739(A)
Project 1B522301A081

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FOREWORD

The work described in this report was authorized under Project 1B52230lA081, Chemical Agent Dissemination (U). The work was started in April 1966 and completed in March 1968. The data are recorded in logbooks C16862, C17183, C17646, and C17680.

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Acknowledgments

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INVESTIGATION OF CHEMICAL SPECIES
AND TEMPERATURES PRESENT IN PYROTECHNIC FLAMES

A number of physical techniques were used to study the reaction products, temperature and rates of combustion of a pyrotechnic mixture containing the agent CS or the simulant 1-methylaminoanthraquinone. These included emission spectroscopy, rapid-scan spectrometry, infrared-absorption spectrometry, interferometry, color and infrared-cine studies, and spectroscopic and thermocouple temperature measurements. Spectroscopic temperature measurements were performed using the two-line, the two-color and the maximum radiant energy wavelength techniques. The difference in these and thermocouple results can be due to the total region observed by each technique. Chemical purity, powder and/or crystal size of the constituents and pressure used to produce the pellet influenced the rate of reaction and temperature. The chemical species observed by emission infrared absorption spectrometry and interferometry were essentially those associated with the combustion of the fuel. Experiments were not sufficiently refined to identify the lesser species and the regions of the combustion zone, however, interferometry and mass spectrometry offer the best techniques. A study of preliminary mass-spectrometry data do show some masses that could be from agent decomposition.

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INVESTIGATION OF CHEMICAL SPECIES
AND TEMPERATURES PRESENT IN PYROTECHNIC FLAMES

I. OBJECTIVES OF THE PROGRAM

The major objectives of the program were as follows:

A. Develop a knowledge of the chemical reactions and heat transmission effects that exist in the combustion region during the reaction of chemical agent-pyrotechnic mixtures.

B. Examine the combustion region spectroscopically in order to determine the chemical species present and the temperature of the combustion zones.

C. Prepare maps of temperature and species concentration as a function of specific combustion regions.

II. HANDLING SYSTEMS AND BASIC EQUIPMENT

The necessary first step in the investigations envisioned in the objectives of this program was to construct an isolation system which would protect personnel from the fumes and agents liberated from the burning pyrotechnics. To insure this protection, a Fisher Isolator Lab (glove box) was modified to serve as an isolation chamber. A hole was cut into the top of this glove box to which was attached a filter chamber with four 8-in. x 10-in. glass fiber filters, type E, Gelman Instrument Company. These filters are oriented edge to edge to form a 16-in. by 10-in. area. A Gelman Hurricane blower, Model No. 16003, was used to exhaust the glove box through the filters into a hood equipped with positive filters. The glove box was further equipped with a 2-3/4-in. diameter optical window through the side. In some work a quartz optical plate was used to cover this opening. The quality of the box and the exhaust system to handle these smokes were tested with 5-gm pellets containing 1-methyl-aminoanthraquinone.

III. COMPOSITION OF PYROTECHNIC PELLETS

The pyrotechnic mixtures to be studied were 40% CS, 25% potassium chlorate, 25% sugar, 10% kaolin. For

preliminary studies, the CS was replaced with the red dye,
1-methylaminoanthraquinone. In addition, "blank" pyro-
techniques were made containing 41.5% potassium chlorate,
41.5% sugar, 17% kaolin.

These mixtures were pressed into pellets of 1/2 in.
diameter and approximately 1 in. in height depending on the
press pressure. Pressures varied from 200 to 1000 lb, dead
weight. In addition, some pellets were prepared from differ-
ent ratios, some with different crystal structure or fineness
and some from different composition to note these influences.
All mixing was done behind a Plexiglas shield; 50 gm of the
mixture was prepared each time. Most of the pellets con-
tained 5 gm of mixture. (Larger pellets were cast later in
the program for some of the infrared work.)

The pellets were combusted in a device in which the
basic holder was precision bore quartz tubing, or in some
cases sapphire tubing which were slightly less than 1/2-in.
inside diameter. A die slightly less than 1/2 in. bore was
constructed so the pellets pressed in it could be inserted
with a close fit into the above holders. This cell was
used for the studies involving emission spectroscopy and
interferometry. A cell using a 1-1/8-in. pellet was
designed with a 29/32-in. long and variable width orifice
for infrared studies. The orifice was a slot approximately
3/16-in. by 2-/32-in. cut into the top of the cell. Two
plates, with their edges parallel to the slot were adjustable,
Figure 13, which permitted variation in the orifice width.

IV. EMISSION SPECTROSCOPIC STUDIES

Some initial emission spectroscopic studies of the
burning pyrotechnic mixtures were performed. The initial
study was performed with the Jarrell-Ash Model 7102,
3.4-meter Ebert mount spectrograph. This instrument is
equipped with a 15,000-line/in. grating and has a reciprocal
dispersion of 5.2 Å/mm in the first order. Additional
studies were performed with the Spex Model 1800, 3/4-meter-
Czerny-Turner mount spectrometer. This instrument is rela-
tively fast optically (f6.3) and has a reciprocal dispersion
of 10 Å/mm.

Iron, chrome, nickel, and copper lines were noted in
the early spectrographic studies. The source, however, was
found to be the hot nichrome wire initially being used to

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ignite the mixture. At these relatively low temperatures, this was an unexpected source of excitation lines.

The most prominent lines of the spectrum were the potassium doublets at 4044.14, 4047.20, and 7664.91, 7698.98 Å and impurities indicated by the intense sodium doublet 5889.95, 5895.92 Å. Traces of rubidium was indicated by the presence of the relatively weak doublet at 7947.60 and 7800.12 Å. The long wavelength doublet for potassium was completely self-reversed indicating an abundance of potassium atoms in the ground state surrounding the reaction zone. Samples were doped with from 1% to 5% RbCl to bring out rubidium lines for higher levels such as the 4201.85 and 4215.56 Å doublet (2.94 and 2.95 eV, respectively). The additional lines did not develop although at the higher additions the burning characteristics of the pyrotechnics were noticeably changed.

Different areas were viewed by the spectrograph, which included the area above the molten interface as well as the plume.

A. Temperature Measurements

1. Two-Line Method

The spectra of the mix without the agent from the 3/4-meter-Czerny-Turner spectrograph were sufficiently "clean" to permit use of the "two-line method" for temperature determination. With the 1-methylaminoanthraquinone or CS present in the pellet this was not the case, therefore, blank pellets were used for the "two-line" measurements. The relatively weak rubidium doublet, 7947.60 and 7800.12 Å (transition levels: 0-1.45 and 0-1.59 eV), was used according to the equation:

$$ T = \frac{(E_1 - E_2)\ (\log e)\ (\frac{1}{k})}{\log\left(\frac{g_1 A_1 \nu_1}{g_2 A_2 \nu_2}\right) - \log\left(\frac{I_1}{I_2}\right)} \qquad (1) $$

where:
E = energy of the upper level
g = statistical weight
A = transition probability
I = relative intensity
ν = wave number, cm^{-1}
sub 1 = wavelength at higher energy level.

For these blank pellets pressed at 500 lb dead weight, temperature was found to be approximately 1450°K and for pellets pressed at 700 lb dead weight, temperatures were approximately 1540°K in the areas above the reaction zone. The region near and including the reaction surface yielded slightly higher temperatures, approximately 1790°K, and in the middle region of the plume approximated 1640°K. It should be noted that these measurements were tentative because large background corrections were necessary and that there is only a small separation of energies in the rubidium doublet, 0.030 eV or 238 cm^{-1}. The very intense potassium doublet, 7664.9 and 7699.0 Å, with the attendant halation and the required background correction, made the relative intensity measurements of the rubidium lines difficult and rather unreliable. It was determined experimentally that doping the pyrotechnics with 0.03% rubidium chloride allowed a decrease in exposure time that completely eliminated the halation background, thus greatly increasing the signal-to-noise ratio. The elimination of the requirement of background correction resulted in values approximately 300°K less than the first measurement and better reproducibility. These values are summarized in Table 1.

Table 1

REPRODUCIBILITY OF SPECTROSCOPIC TEMPERATURE MEASUREMENTS

Blank Pyrotechnics Pressed at 700 lb T (°K)	Red Dye Pyrotechnics Pressed at 300 lb T (°K)
1140	1230
1140	1300
1200	1270
1270	1200
1150	
1080	
1070	
1115	

Later experiments in which simultaneous thermocouple measurements were made, to compare with spectrographic measurements for blank pellets, are illustrated in Figures 1 and 2. In these experiments, the spectroscopic results are
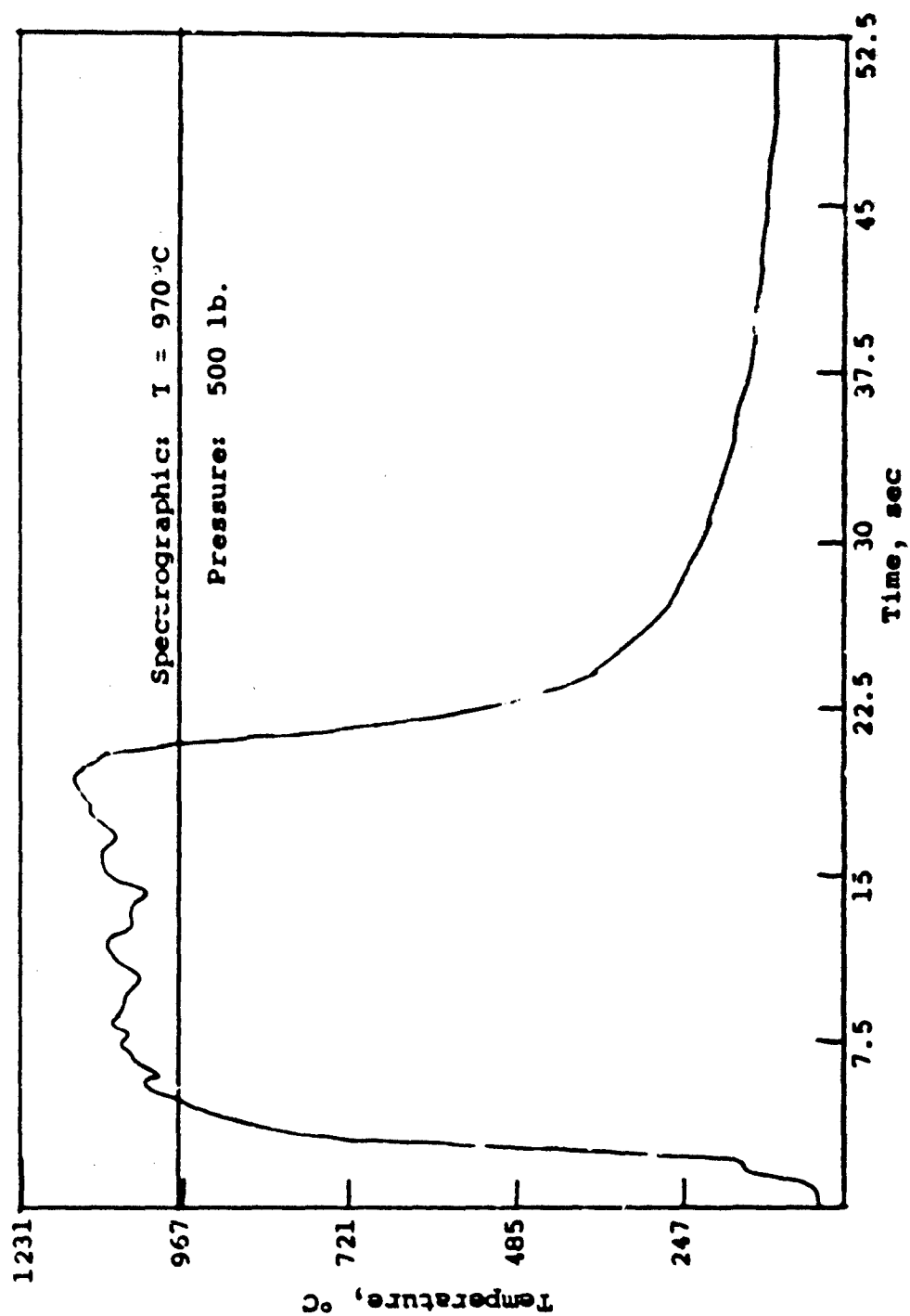
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Figure 1. A COMPARISON OF SPECTROGRAPHIC AND THERMOCOUPLE
TEMPERATURE MEASUREMENTS (PYROTECHNIC WITHOUT ANY AGENTS)
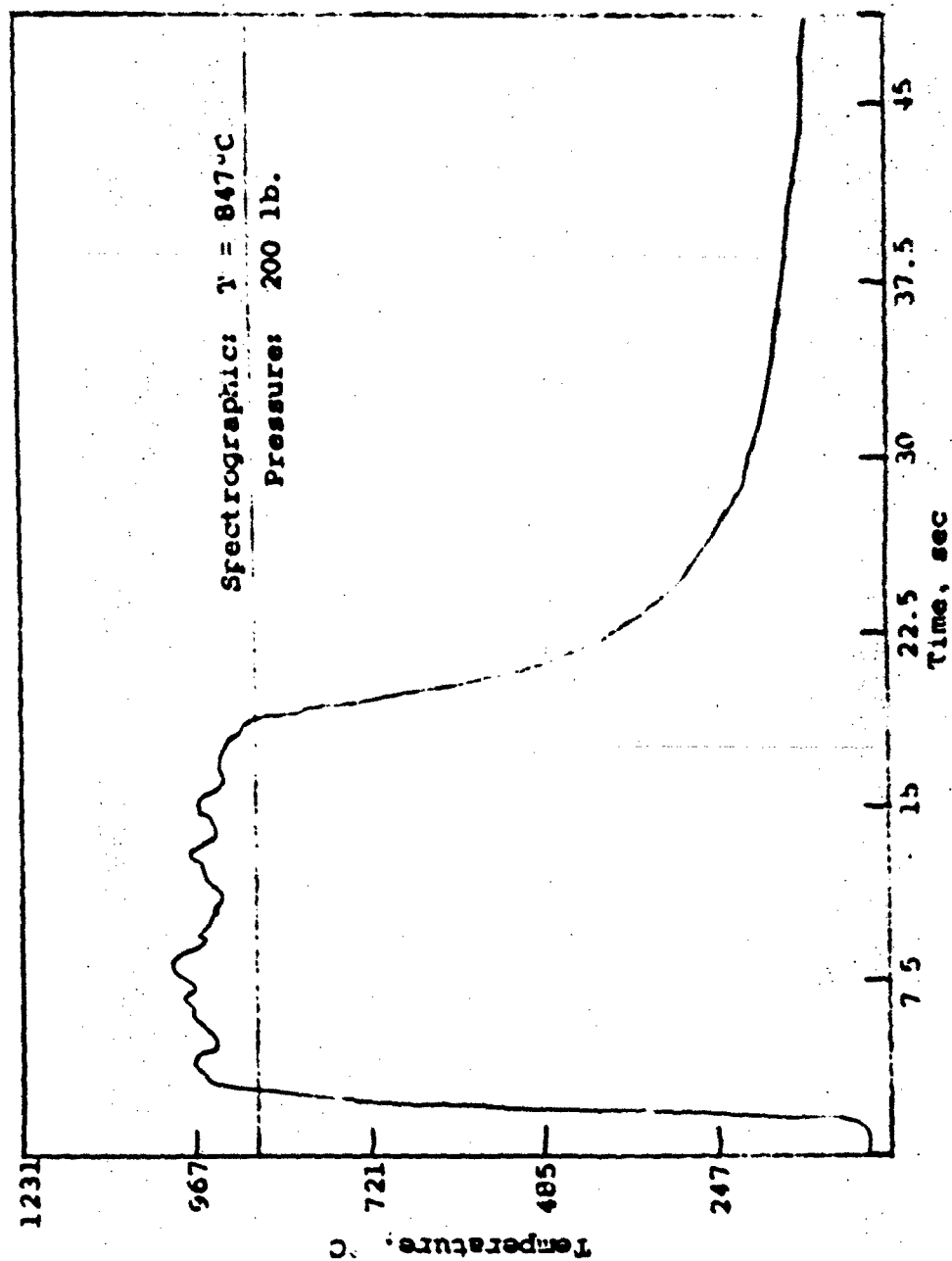
Figure 2. A COMPARISON OF SPECTROGRAPHIC AND THERMOCOUPLE
TEMPERATURE MEASUREMENTS (PYROTECHNIC WITHOUT ANY AGENTS)

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lower than for the thermocouple measurements and lower than those listed in Table 1.

2. Two-Color Method

With the agent or the 1-methylaminoanthraquinone in the pyrotechnic mix, a strong continuum is present, which prohibits use of the two-line method. The rubidium lines do not appear above this strong background so other approaches than the line-ratio method for temperature measurements were required. The two-color method depends on the radiant energy intensity at two different wavelengths. This gives the slope of the black body curve, which is a function of temperature. This relation is calculated from the following expression:

$$T = \frac{C_2\left(\frac{1}{\lambda_2} - \frac{1}{\lambda_1}\right)}{\ln\left(\frac{A(\lambda_2)}{A(\lambda_1)} \cdot \frac{\varepsilon(\lambda_2)}{\varepsilon(\lambda_1)} \cdot \frac{I(\lambda_2)}{I(\lambda_1)} \cdot \left(\frac{\lambda_1}{\lambda_1}\right)^5\right)} \qquad (2)$$

where:
C_2 is the second radiation constant
$A(\lambda)$ is an instrumental constant
λ is the wavelength
(λ) is the emissivity at λ
$I(\lambda)$ is the intensity at λ.

Simultaneous thermocouple and color temperature readings were taken from which it was noted that the temperatures from the two-color techniques were always higher than the thermocouple temperatures. Color temperatures were measured at 4000 to 4100 Å and 4000 to 4200 Å. In all these measurements, the emissivity ratio

$$\frac{\varepsilon(\lambda_2)}{\varepsilon(\lambda_1)}$$

was assumed to be 1.0, but it appeared from the discrepancies that the ratios should have been 1.42 for 4000 to 4100 Å and 1.93 for 4000 to 4200 Å. Re-exposure of spectra with longer exposure times brought out the weak band structures in this region of the spectrum for which these correction factors were necessary.

Gaydon and Wolfhard[1] have reported that the color temperature of a candle flame is about 100°C higher than its true temperature due to the change in emissivity with change in wavelength.

It should be noted that the thermocouple measurements represent the temperature (if the equilibrium between the hot gas and the thermocouple is reached) at a given point in the pyrotechnic, as a function of time, whereas the optical measurement represents a measure of the radiation from a relatively large area and cover the whole burn time of the pellet.

Measurements by thermocouple and spectroscopic methods were made on pellets containing the simulant and the agent. Figures 3 and 4 represent the simulant, and Figure 5 represents the burn with CS present. In these examples the spectroscopic temperature was generally higher than the thermocouple. The samples appeared to burn much more unevenly with the added organic materials present than when absent. Also, in general, pellets pressed at a higher pressure burned at higher temperatures.

3. Maximum Radiant Energy Wavelength

Six measurements were made in the infrared region using the Perkin-Elmer rapid-scan spectrometer. The black body maximum was noted at 2.24μ in each case. This maximum corresponds to 1300°K. A globar at 1303°K measured with an optical pyrometer, gave the same wavelength of maximum radiance.

B. Chemical Species Detected

From the emission technique only a few emission species were observed. These included the atomic species K, Na, Rb, and the diatomic species OH, NH, CN, CH, and C_2. The Na and Rb were the major impurities in the potassium chlorate. Only a few bands were observed to identify the diatomic species which, in general, were the most persistent bandheads. These were as follows:

---

[1] A. G. Gaydon and H. G. Wolfhard, Flames, Their Structure, Radiation and Temperature, Chapan and Hall, Ltd., London, 1960.

Figure 3. A COMPARISON OF SPECTROGRAPHIC AND THERMOCOUPLE TEMPERATURE MEASUREMENTS (PYROTECHNIC WITH RED DYE)

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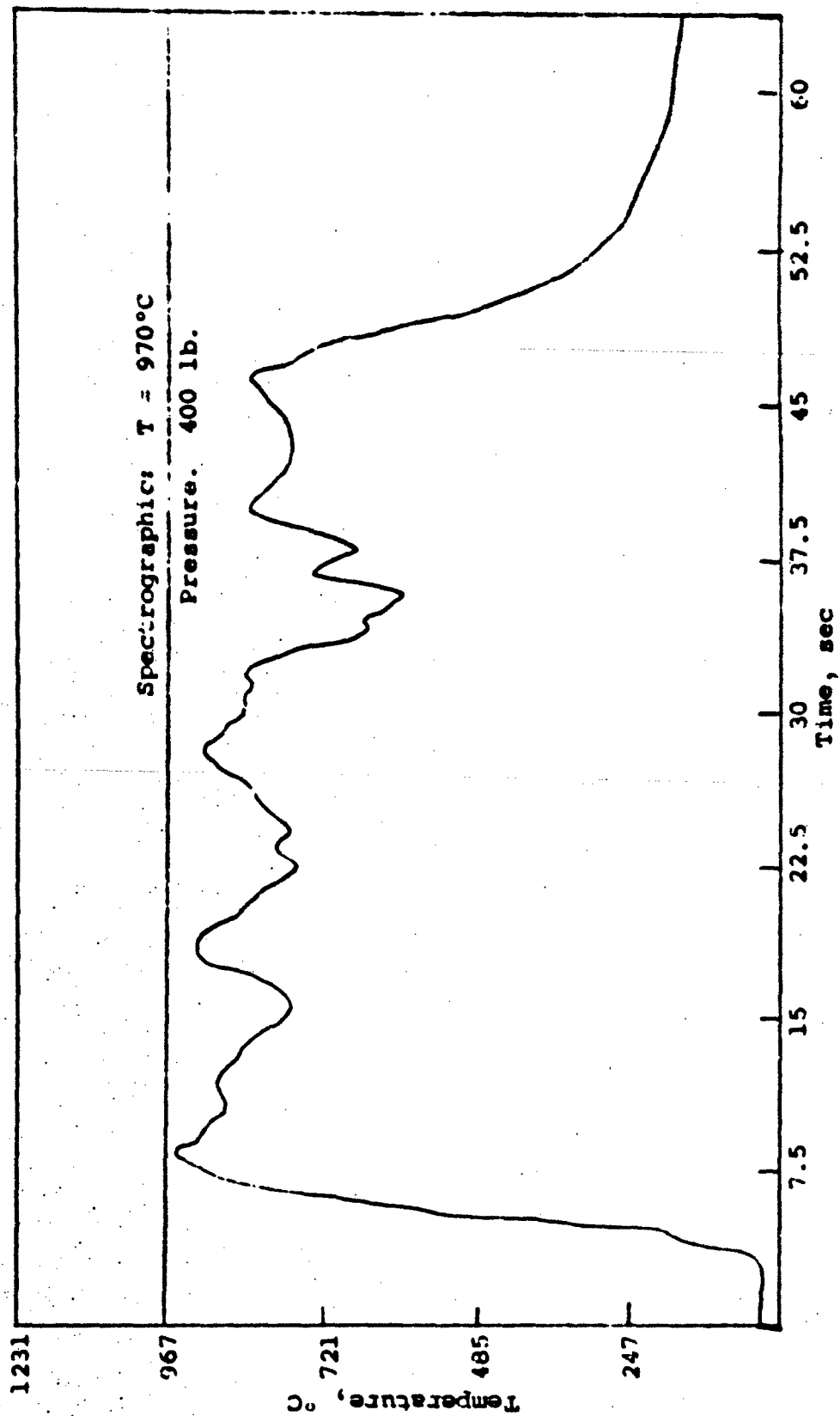
Figure 4. A COMPARISON OF SPECTROGRAPHIC AND THERMOCOUPLE
TEMPERATURE MEASUREMENTS (PYROTECHNIC WITH RED DYE)

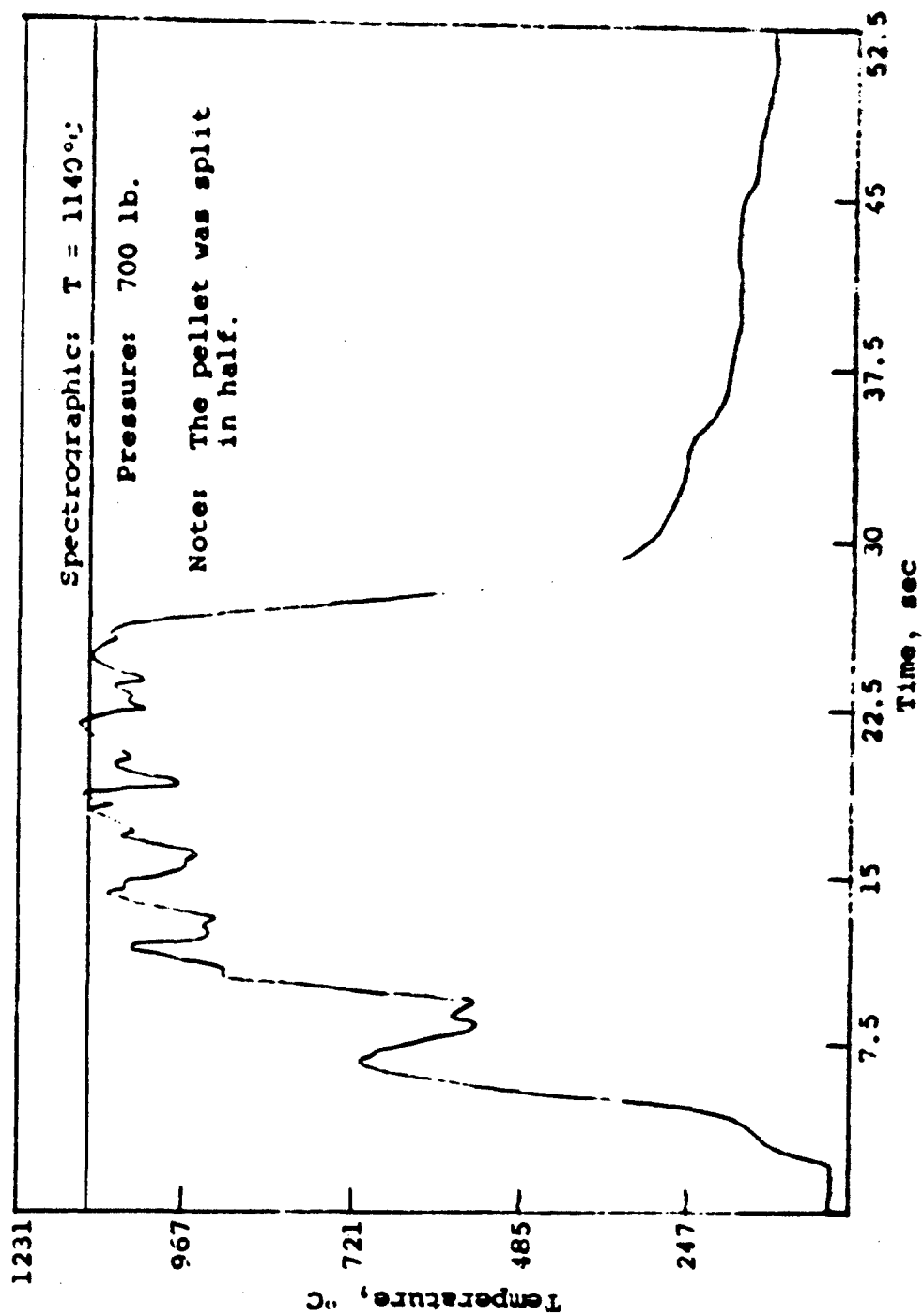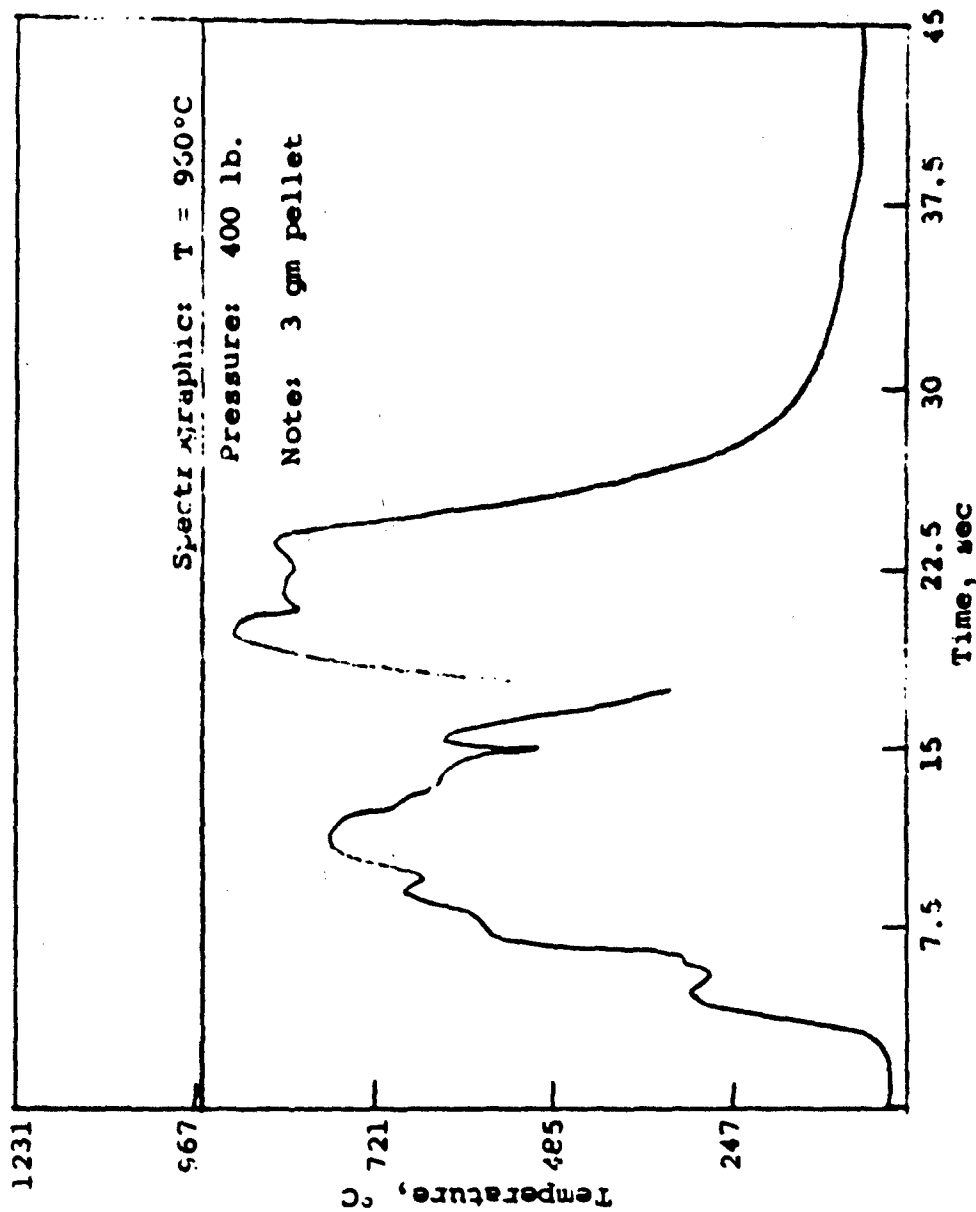Figure 5. A COMPARISON OF SPECTROGRAPHIC AND THERMOCOUPLE
TEMPERATURE MEASUREMENTS (PYROTECHNIC WITH CS)

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OH   bandhead observed at 3064 Å;

NH   two bandheads observed at 3360 Å
     (0-0 transition) and at 3370 Å
     (1-1 transition);

CN   two band sequences observed at 3383.4 Å
     (0-0 sequence) and 3590.4 Å
     (1-0 sequence);

CH   violet degraded bandhead observed at 4312.5 Å
     and a red degraded bandhead at 3872 Å
     (partially obscured by CN bands);

C_2 bandhead at 5165.2 Å
     (0-0 transition) and at 4737 Å
     (1-0 transition);

K_2 weak bands at 3575, 3552, 3559, and 3541 Å.

There were a few additional weak band structures, which we were unable to identify from our atlases. The emission for a CS pyrotechnic is shown in Figure 6.

C.   Time Resolved Spectra - Perkin-Elmer Rapid-Scan Spectrometer

The Perkin-Elmer Model No. 108 rapid-scan spectrometer was used in the near ultraviolet-visible to the infrared region. The S-1 response photomultiplier was used as the detector in the shorter wavelengths, the PbS detector was used for the $1-\mu$ to $3-\mu$ region, and the bolometer was used for the $1-\mu$ to $7-\mu$ region.

In the ultraviolet-visible region the results were the same as previously observed, only the buildup and decay of species could be noted as the reaction proceeded.

In the $1-\mu$ to $7-\mu$ region, the most detail was observed. A globar at approximately the same temperature was used as a reference. The spectra is shown in Figures 7 and 8, in which the absorption bands for water, 2.8μ, carbon dioxide, 4.3μ, and for polystyrene, 3.3μ are shown. The emission bands for water and carbon dioxide stand out clearly in Figure 9 and these two emissions are superimposed on the black-body curve caused by the hot simulant in Figure 10.
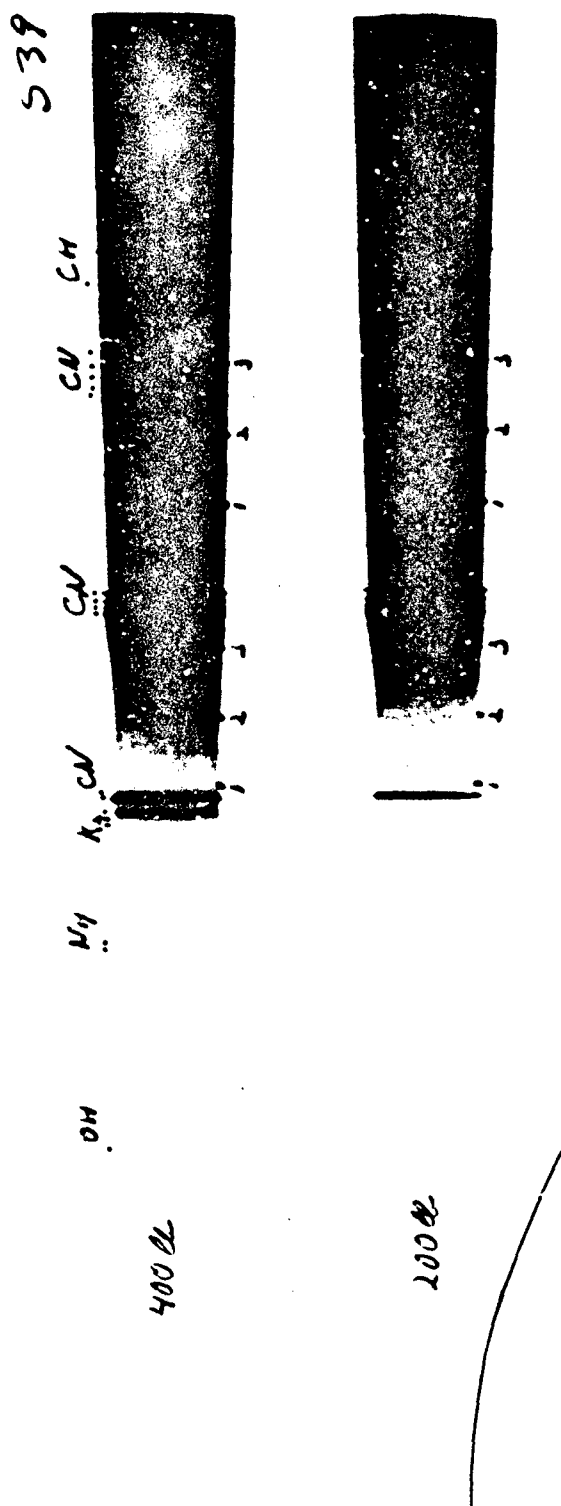
Figure 6.   THE EMISSION SPECTRA (2200 to 4600 Å) OF PYROTECHNICS
CONTAINING CS (3 gm PELLETS)
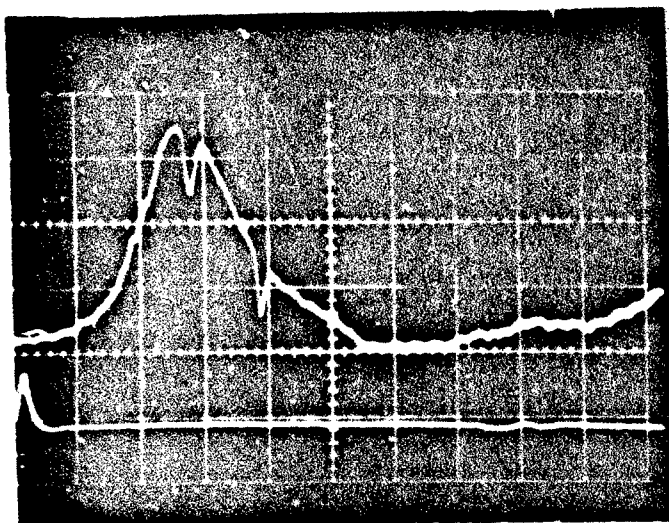
Figure 7

RAPID SCAN INFRARED GLOBAR REFERENCE SPECTRUM.
WATER (2.8μ) AND CO_2 (4.3μ) ABSORBTION BANDS MAY BE NOTED.
GLOBAR TEMPERATURE 1030°C.
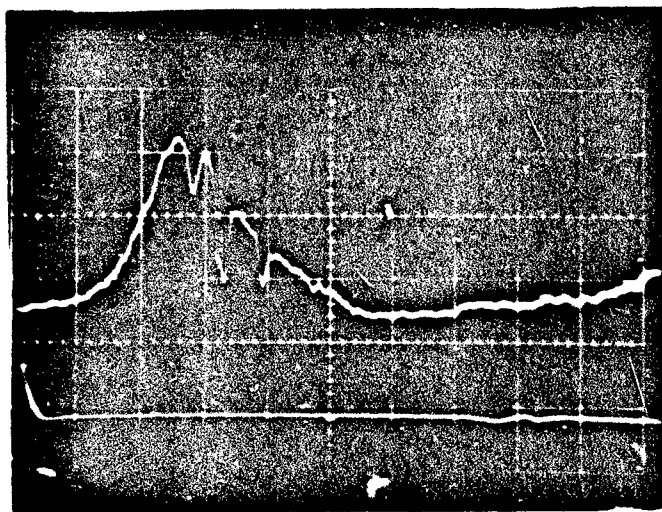
Figure 8

RAPID SCAN INFRARED GLOBAR AND POLYSTYRENE REFERENCE SPECTRUM.
WATER (2.8μ), CO_2 (4.3μ) AND POLYSTYRENE (3.3μ)
ABSORBTION BANDS MAY BE NOTED.

23
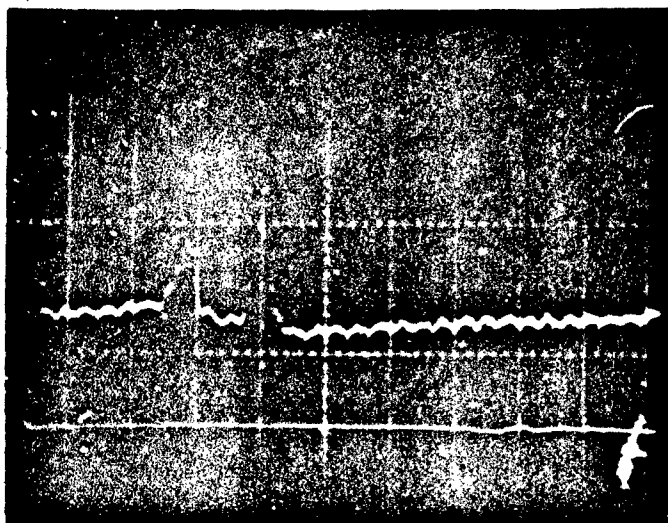
Figure 9

RAPID SCAN INFRARED SPECTRUM OF A PYROTECHNIC
WITHOUT ANY AGENTS.   WATER (2.8μ) AND CO_2 (4.3μ)
EMISSION BANDS MAY BE NOTED.
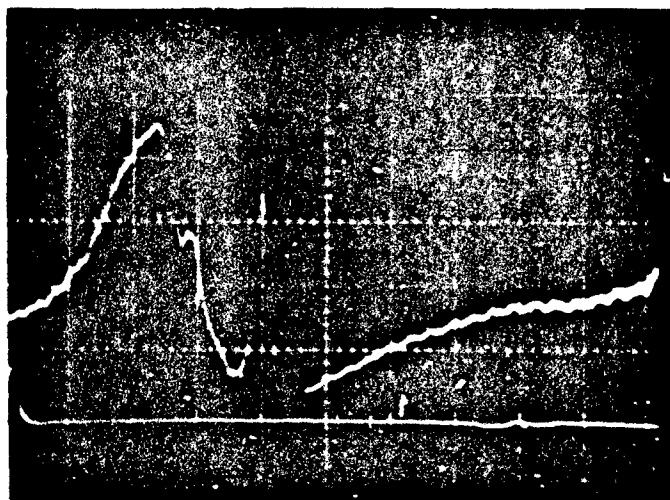
Figure 10

RAPID SCAN INFRARED SPECTRUM OF A PYROTECHNIC WITH RED DYE.
WATER (2.8μ), CO_2 (4.3μ) EMISSION BANDS
AND THE BLACK BODY CURVE MAY BE NOTED.
ESTIMATED TEMPERATURE: APPROXIMATELY 1000°C.

Better resolved spectra showed additional bands in the 3-μ to 5.5-μ region, which, from infrared reference charts, would indicate species, such as $-CH_2$, $-CH_3-$, $-O-CH_2-O-$, $-NH_2$, and $-N-CH_3$.

Since Pyrex is transparent to approximately 1μ, Lucalox, a ceramic of polycrystalline Al_2O_3 (synthetic sapphire) that is transparent up to about 8μ was used to study the combustion region.

D. Particle Size Effects

The initial chemicals used for the pyrotechnic mixtures were supplied by Edgewood Arsenal. These were the quality as required by the Military Specifications. The new mixes were prepared from more reagent grade chemicals. Differences in burning characteristics finely ground with a mortar and pestle were noted and the ash appeared to be more coarse.

More specific and continued observations were not made because the Edgewood chemicals were used up.

V. MOTION PICTURE STUDIES

The width of the molten zone and the rate of reaction in terms of length per unit of time was determined for 1/2-in. diameter pellets. Percent of CS agent in the composition was 40%. Red dye simulant was added in 1/4%, 1/2%, and 1% by weight in order to form a bright red band of the molten zone. The percent produced a faint pink color to the pellet. After several test samples, it was decided that the 1/4% red dye composition produced sufficient color intensity for the motion picture study.

The orifice for these reactions was 3/16 in. in diameter and gave a pressure of about 7 lb/sq in.

Both infrared and color film pictures were taken. These showed a definite zone of separation between the burned and unburned parts and all the combustion appeared to take place at this zone. Pellets with no dye added had a molten zone of 0.76 mm and a vertical movement of 0.50 mm/sec. With 1% red dye, the zone thickness was the same but the rate of reaction was slower; 0.35 mm/sec. The small amount of simulant did change the rate of combustion. Different combustion rates had been noted previously.

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The combustion down the pellet was quite uniform, however, the infrared film showed various degrees of brightness during this process. It was not possible to distinguish between the molten and combustion (reaction) zone.

VI. ABSORPTION SPECTROMETRY STUDIES

A brief study of the hot gases above the orifice was performed with the Perkin-Elmer Infracord Model 137 spectrometer. The region examined was the clear area, about 1/2 in. in length, just above the orifice before the agent began to condense and form the smoke. A rectangular passage, 4-1/2-in. by 5-1/4-in. by 3-ft outside measurement, was constructed from 3/16-in. clear polystyrene plastic sheet. This device would fit into the 4-1/2-in. cell space of the instrument and conduct the fumes above the reference light path and into the fume hood, Figure 11. Sodium chloride windows were used for most of the studies, although initially a pair of barium chloride windows were used until the rock salt windows were received. Most of the air needed by the hood passed through this device, and no contamination accidents resulted.

One of the difficulties experienced was the rather frequent self-extinguishing of the combusting pyrotechnic. It was necessary to place the samples in a partially horizontal position, then sufficient molten material would flow into and block the orifice. This was especially severe when three 1-in. pellets were held in one case to have sufficient reaction time to obtain a few microns of scan. These samples were burned in a heavy brass case. Should time have permitted the spectrometer could have been set at a 30° to 45° angle from horizontal and the tube rebuilt so the pellets would be more nearly vertical.

The use of the small chamber with 1/2-in. diameter pellets, details of construction are shown in Figure 12, with the 3/16-in. diameter orifice resulted in too short an optical path to produce sufficient signal. A 1/2-in. long slot, however, began to produce a reasonable structure. A larger chamber was designed and constructed, shown in Figure 13, for 1-1/8-in. diameter by 1-in. pellets. The slot for this chamber was 29/32 in. long and could be adjusted in width from 0 to nearly 3/16 in.

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SODIUM CHLORIDE
WINDOW

SAMPLE SLIT

REFERENCE
SLIT
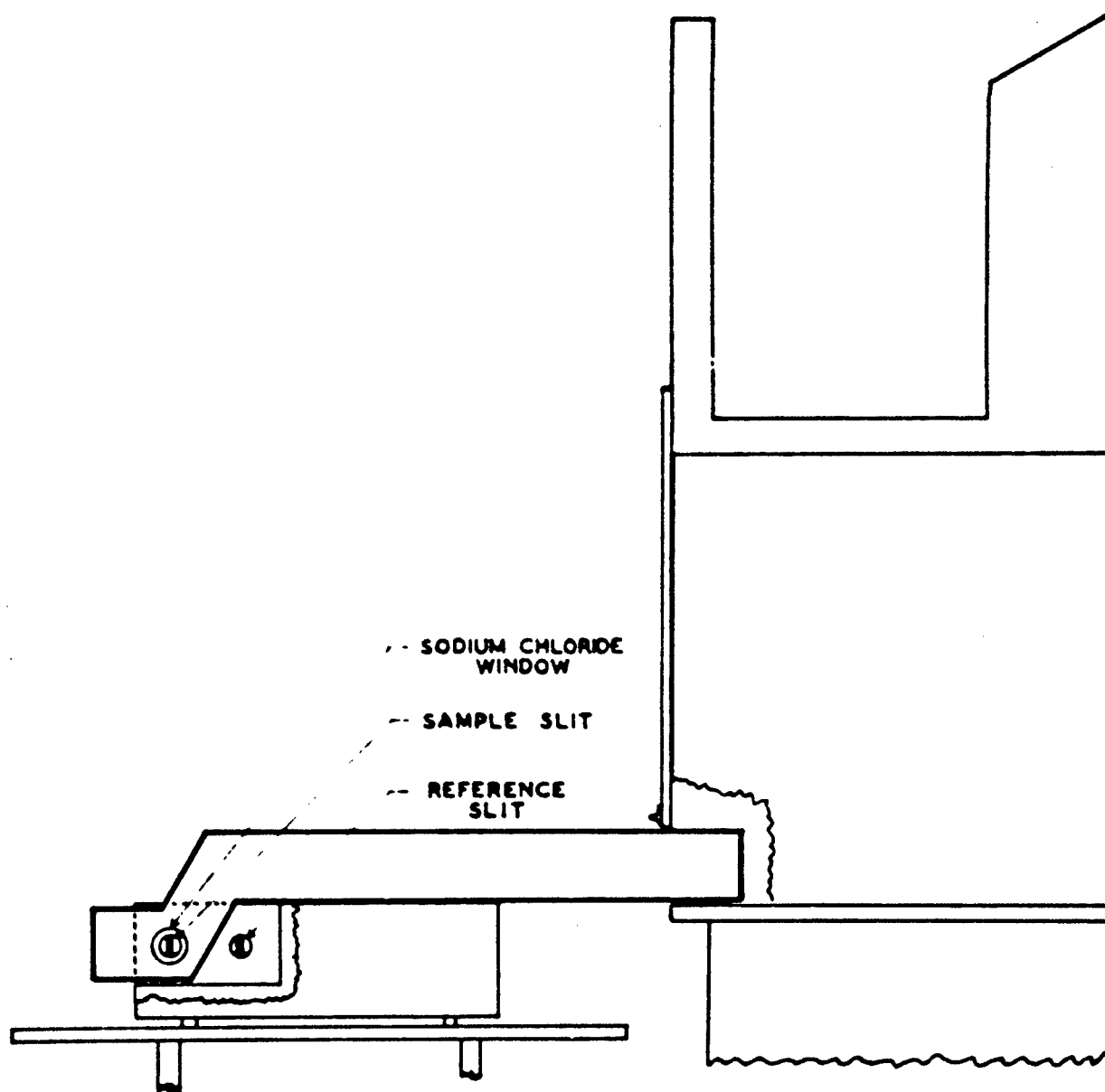
Figure 11.   VENT SYSTEM FOR IR STUDIES
ON BURNING PYROTECHNICS

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TEFLON "O" RING. 0.364 ID, 0.585 OD.

PRECISION BORE QUARTZ TUBE.
0.500 ID, 0.625 OD.

"O" RING. NO. 112-8307
PRECISION RUBBER PRODS. CORP.
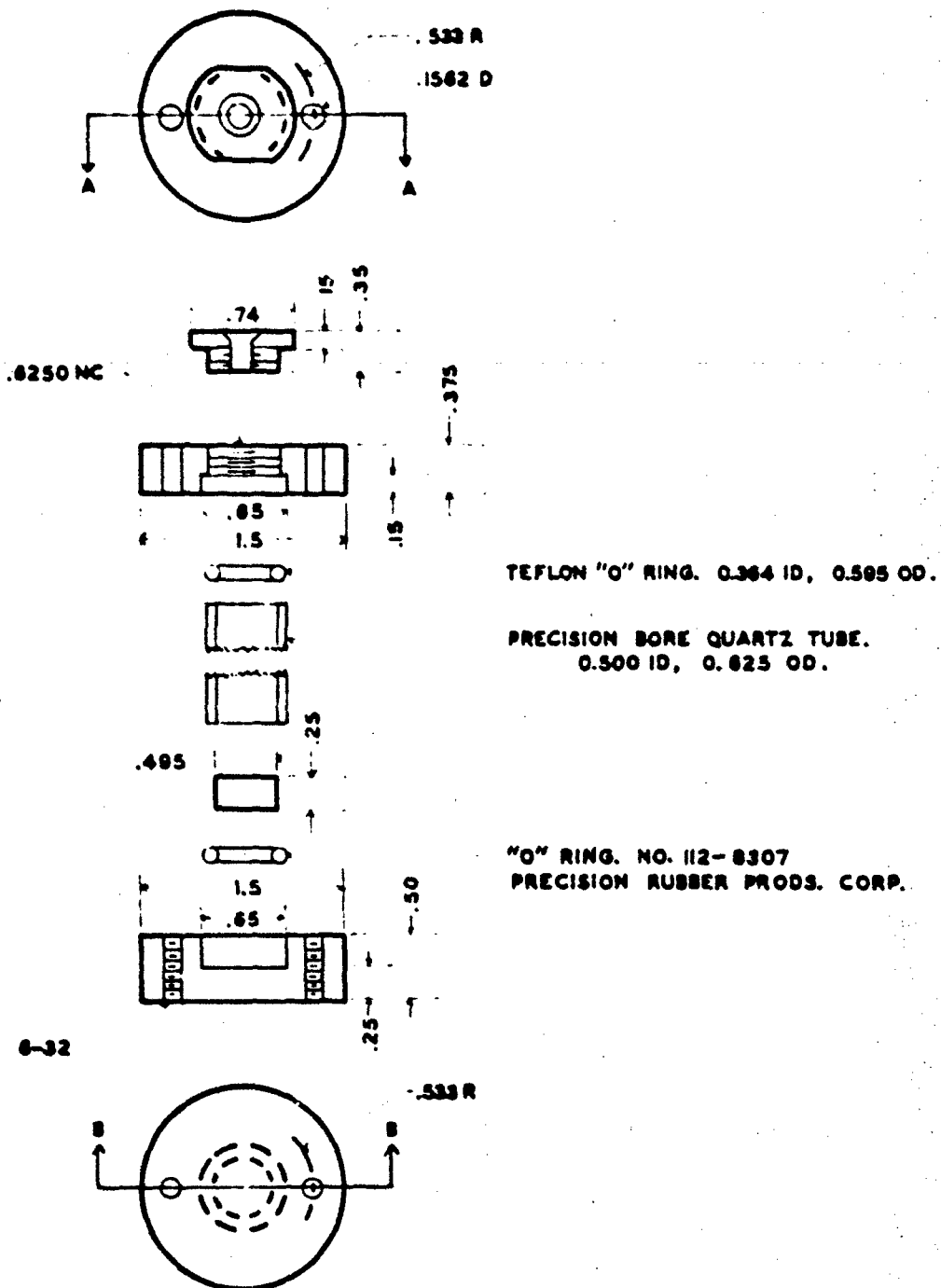
Figure 12.   CHAMBER FOR 0.5-in. DIAMETER
PYROTECHNICS INTERCHANGEABLE BODY AND ORIFICE

30
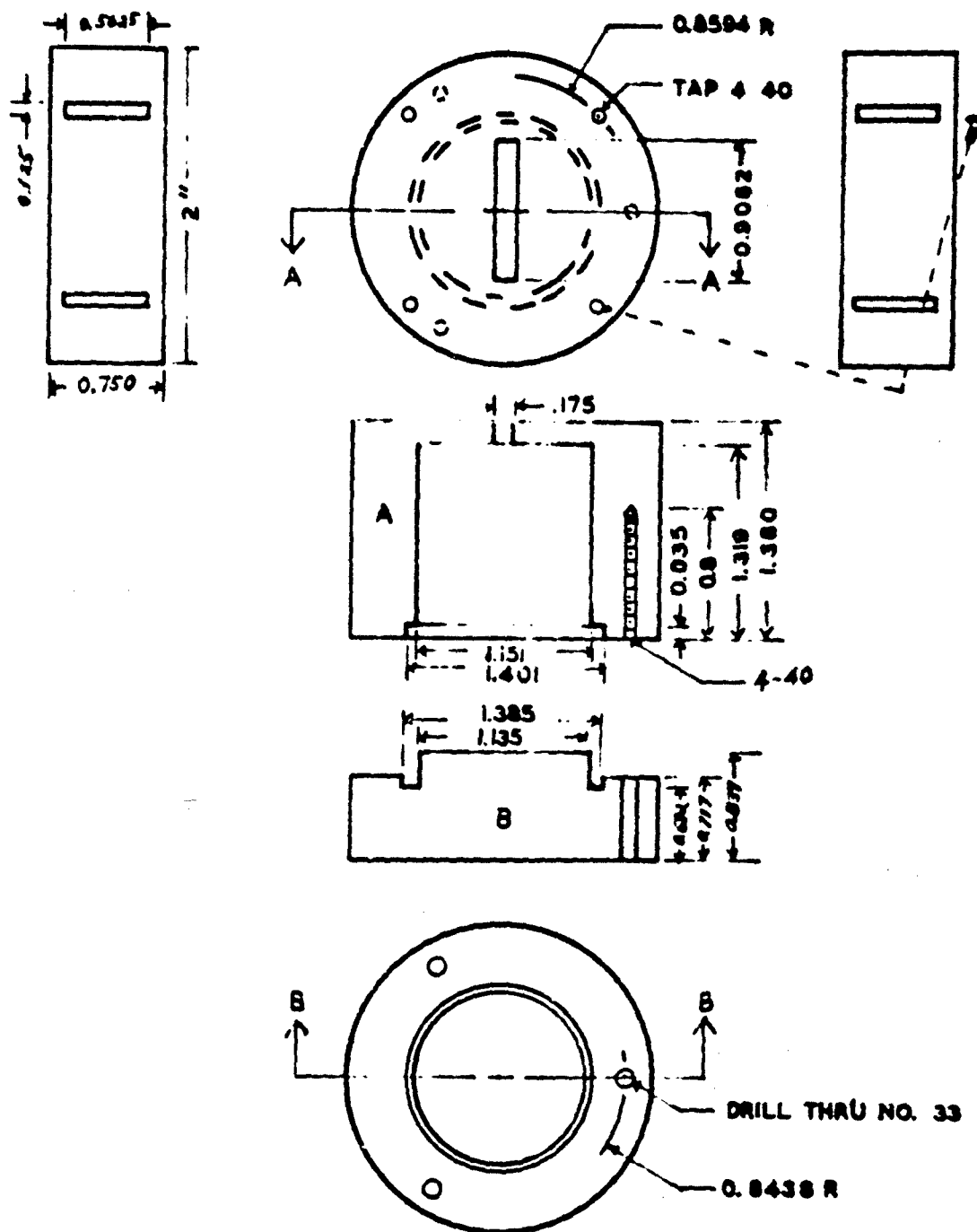
Figure 13. CHAMBER FOR BURNING
1-1/8-in. DIAMETER PYROTECHNICS

Attempts to pass the gases through a 3-in. gas cell were not successful, since too much condensation took place resulting in light scatter. Simple attempts to heat this cell for this gas flow from the burning pellet were not successful. Condensation still occurred on the windows.

Examples of spectra of the flowing spectra are given in Figures 14 and 15. In Figure 14, the loss of intensity was the result of BaCl$_2$ windows and was one of the first spectra. In part, the differences are believed to be due to operating difficulties and condition and quality of the burn. A comparison of Figure 15 with the spectra of CS in a KBr pellet, Figure 19, shows some of the major structures. This brief study was preliminary and more refinements are needed.

In order to have a reference, a special cell equipped with sodium chloride windows, heating mantle and a thermocouple was prepared in order to obtain spectra of pure CS in the vapor state. From this study it appeared that for a single sample cycled from 150°C back down to 25°C, then back up to 150°C, no appreciable degradation took place at 150°C.

Examples of spectra from the CS vapor under partial vacuum at room temperature, 70°C, 100°C, and 150°C, are shown in Figures 16, 17, and 18. Reference spectra using KBr disc techniques were prepared for CS, the fuel (sugar) and the oxidizer (KClO$_3$), Figures 19, 20, and 21, respectively.

Table 2 summarizes the prominent features of these spectra. Some of the bands are missing when compared to the CS in the KBr pellet. In general, these are the weaker bands for which the concentration was too low to detect, or the instrument was operated at too low sensitivity. Added structures in the hot gas from the flare were combustion products.

VII. QUENCHING EXPERIMENTS

A few experiments were performed in which the burning pyrotechnic was quenched in liquid nitrogen. It is interesting to note that the sample separated into three distinct parts, the nonreacted portion, the reaction or molten zone, and the spent or reacted portion. This was not an accidental happening but consistently occurred with several samples.
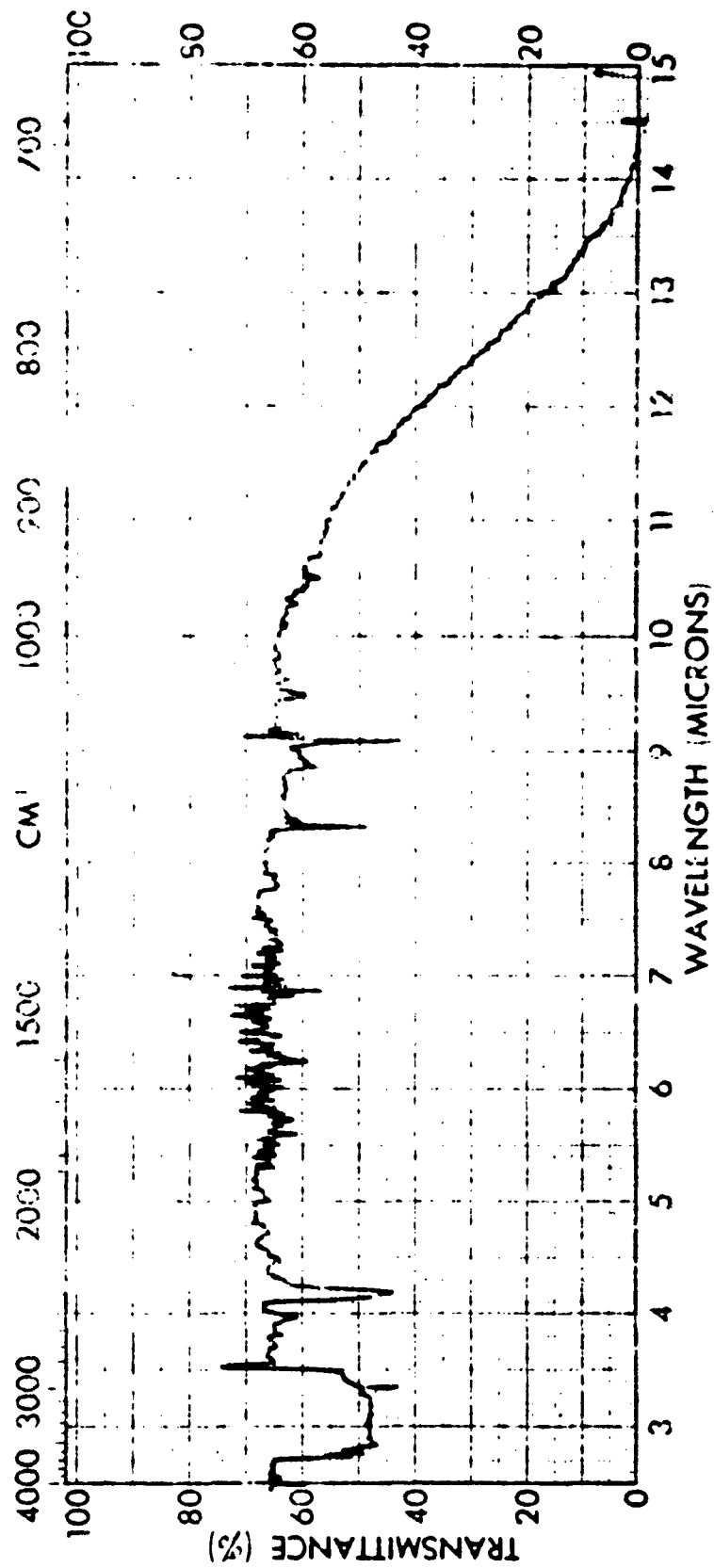
Figure 14. IR SPECTRA OF GAS FLOW FROM BURNING CS PYROTECHNIC

33
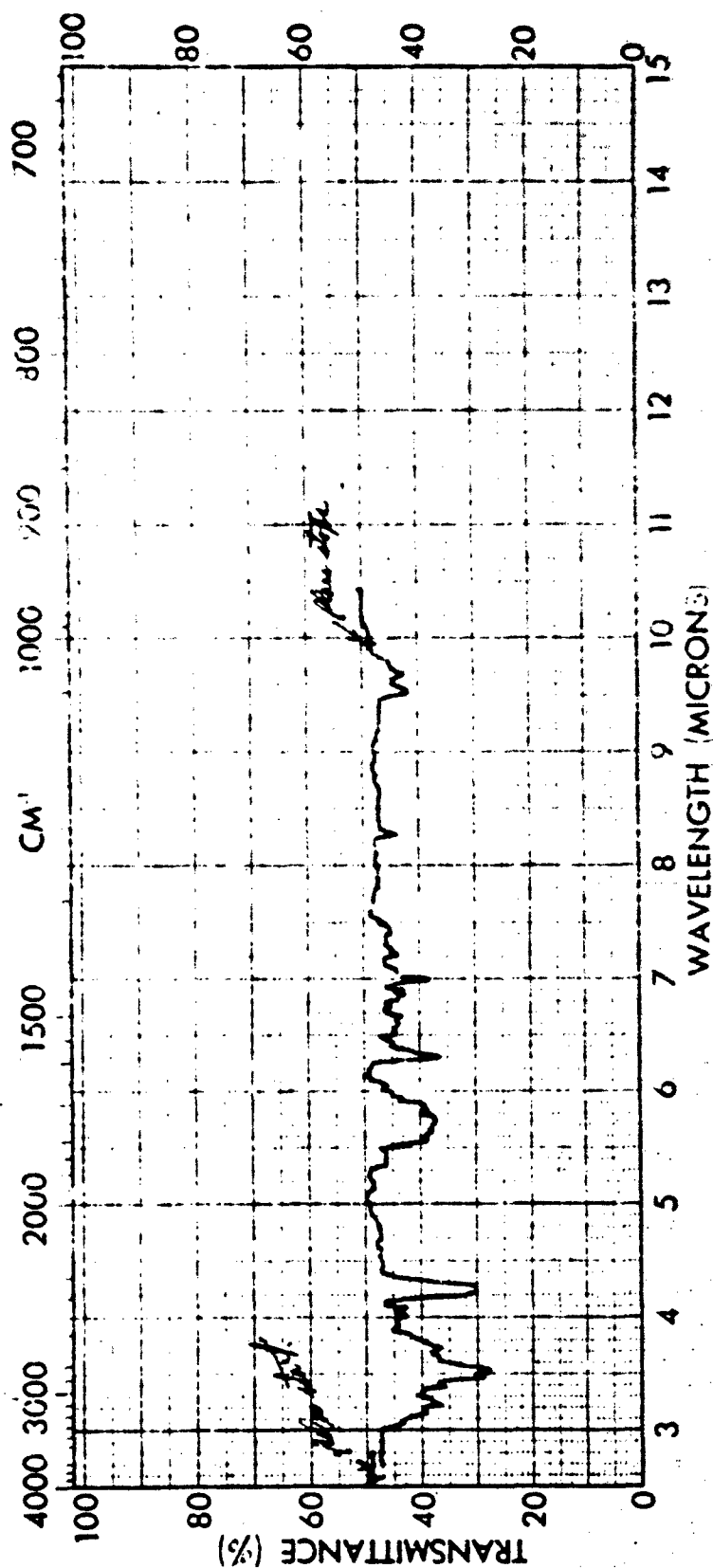
Figure 15. IR SPECTRA OF GAS FLOW FROM BURNING CS PYROTECHNIC

34
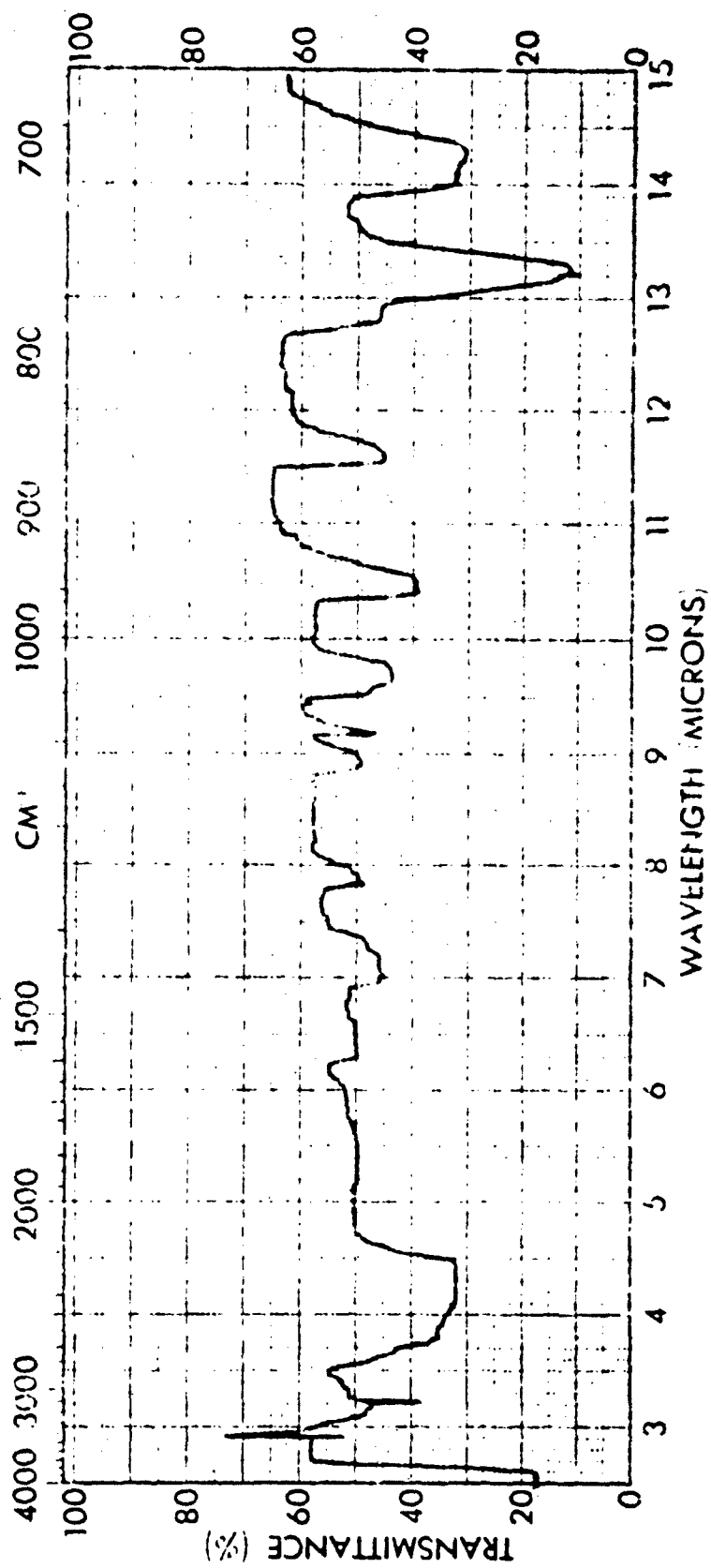
Figure 16. IR SPECTRA OF CS VAPOR AT 25°C

35
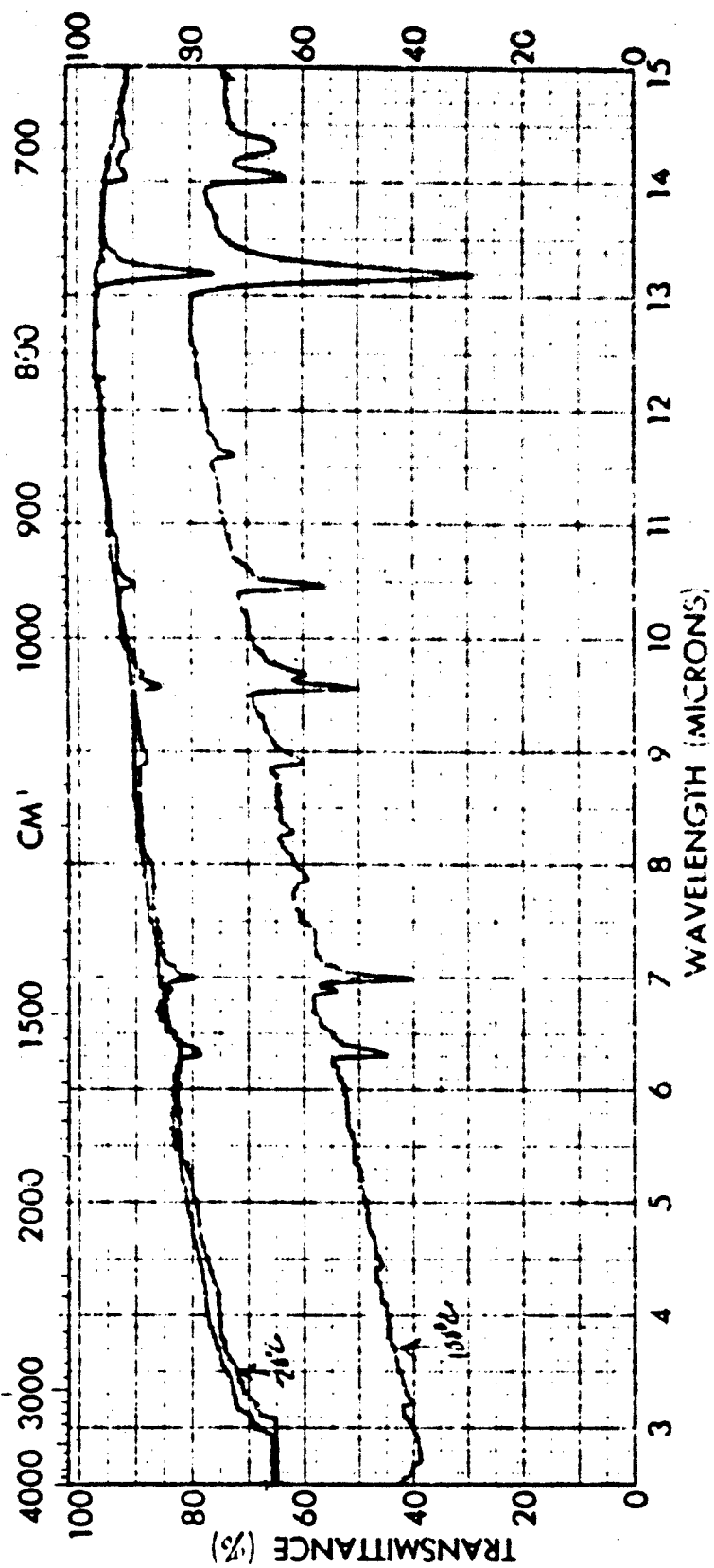
Figure 17. IR SPECTRA OF CS VAPOR TEMPERATURES AS NOTED
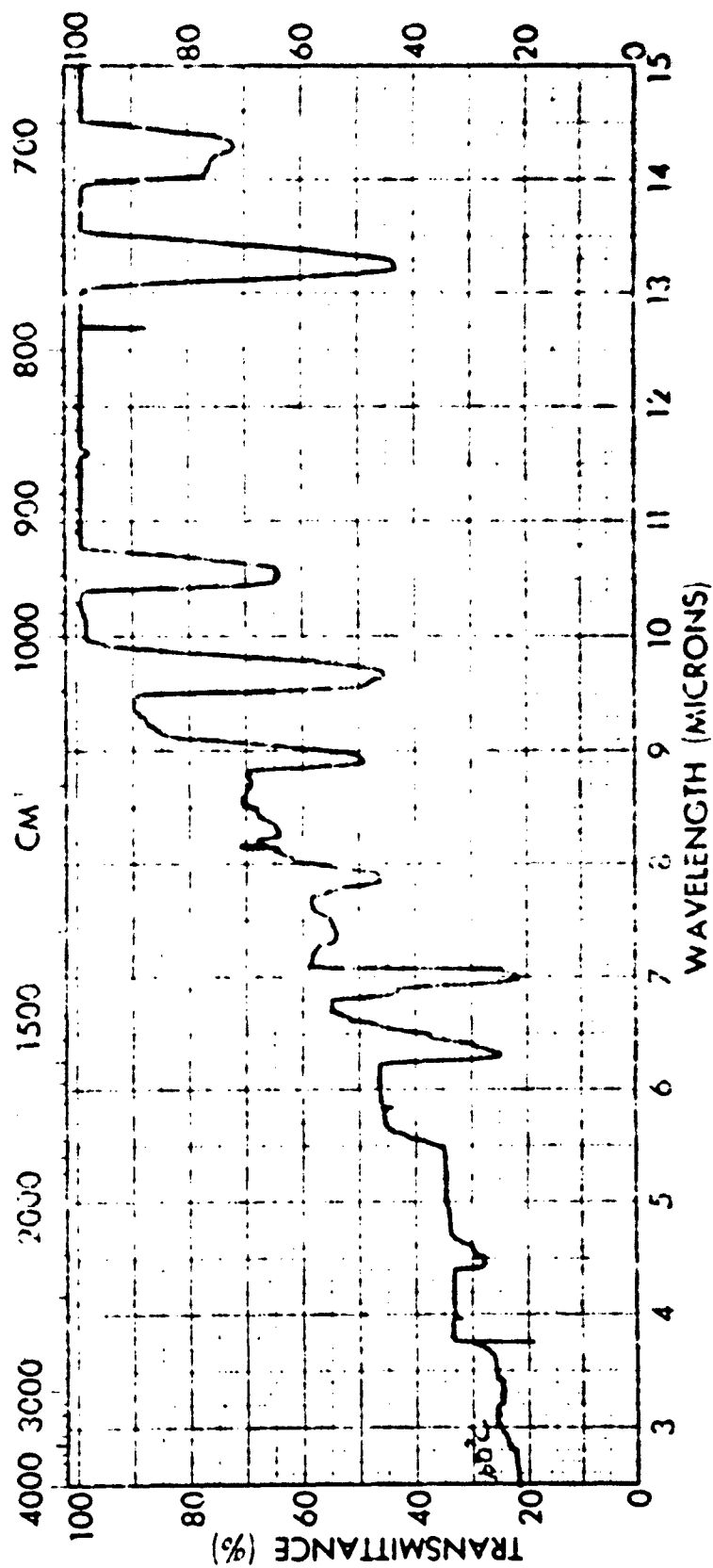
Figure 18. IR SPECTRA OF CS VAPOR AT 150°C

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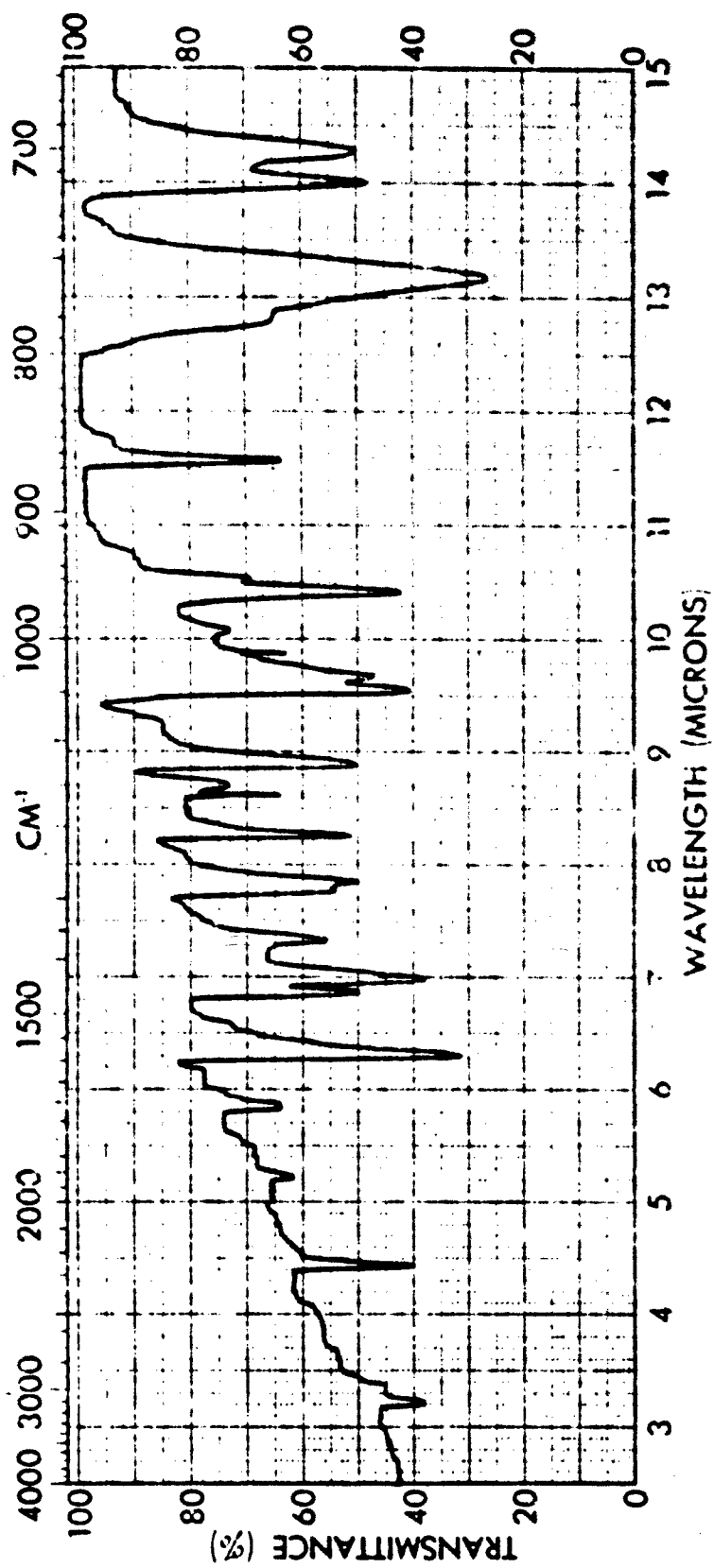
Figure 19. IR SPECTRA OF CS IN KBr DISC
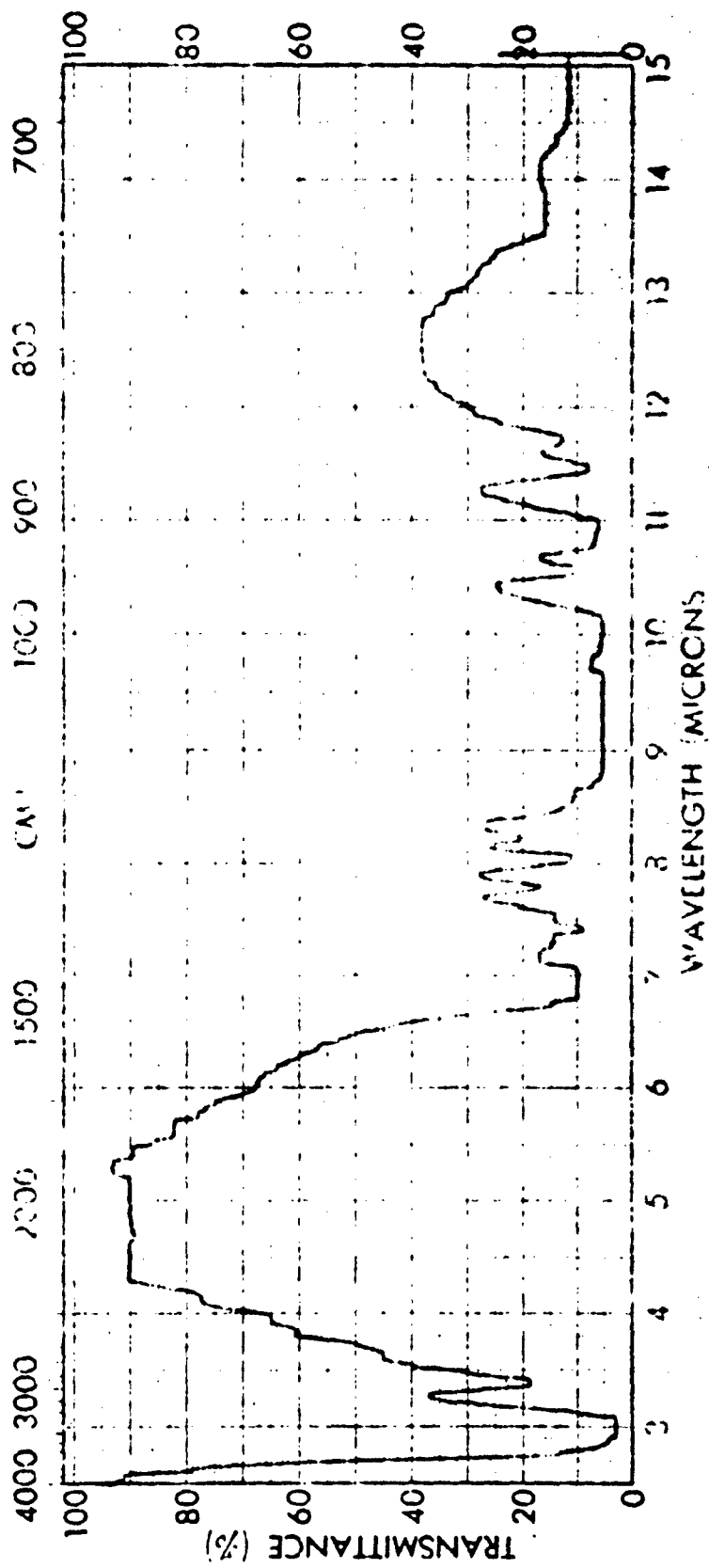
Figure 20. IR SPECTRA OF FUEL (SUGAR) IN KBr DISC
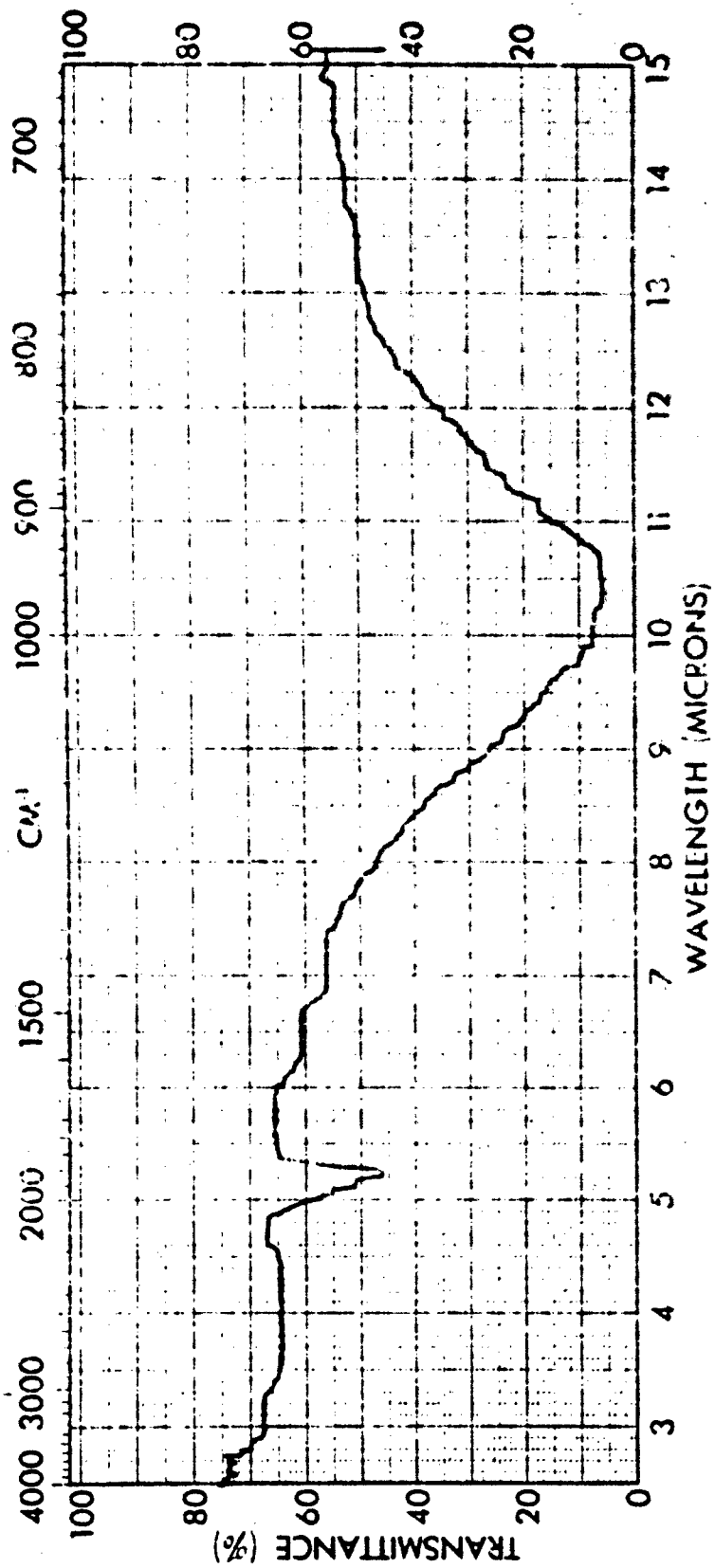
Figure 21. IR SPECTRA OF OXIDIZER ($KClO_3$) IN KBr DISC

40

Table 2

ABSORPTION PEAKS, μ

CS in KBr Disc	Burning Flare	CS Vapor			
		25°C	70°C	100°C	150°C
3.20	3.20	3.20			
	3.45				
	3.52	3.50			
	3.75				
	4.25				
4.41					
		4.50			4.45
5.22					
5.85	5.85				
6.30	6.30		6.30	6.30	6.30
6.88				6.88	6.88
6.97	6.97	6.97	6.97	6.97	6.97
7.32					6.32
7.75				7.75	7.75
7.85		7.85			7.85
8.27	8.27			8.27	8.27
8.70					8.70
8.90		8.90	8.90	8.90	8.90
9.55	9.55	9.55	9.55	9.57	9.55
9.68	9.68	9.68	9.68	9.70	9.68
10.07					
10.40		10.40	10.40	10.45	10.45
10.52		10.52			10.55
11.57		11.57		11.60	11.60
12.80		12.80			
13.18		13.18	13.18	13.20	13.25
14.00		14.00	14.03	14.03	14.03
14.30		14.30	14.30	14.30	14.30

The reaction zone was treated with CCl_4 and CH_3OH to extract the agent. The infrared absorption spectra of the CCl_4 extract was that of the CS agent and the ultraviolet spectra indicated its presence in the CH_3OH solution.

Later the agent was found in both the reaction zone and the ash through the qualitative studies with the mass spectrometer.

VIII.   INTERFEROMETRY STUDY

In the process of looking for more sensitive methods to study the reaction zone, interferometry was briefly explored. A Michelson-type interferometer in the $4-\mu$ to $40-\mu$ range was used through the courtesy of Block Associates, Inc. The purpose of this exploratory effort was to see if there was sufficient signal to detect any species, and possibly recognize them from known wavelengths. Some interpretations were possible from the preliminary interferograms.

Figure 22 is the emission spectrum from the interferogram from a burning pyrotechnic pellet enclosed in a sapphire sleeve with the proper sized opening in the brass cap to produce the proper pressure. The pellet combusted properly with no flame. Figure 23 was obtained in the same manner except that a rock salt window was used between the pyrotechnic and the interferometer sensor to prevent any escape of the smoke into the room.

The two main species appear to be OH indicated by an OH band at about 5.7μ and the CO_2 at 15μ. This band at 5.7μ can also be due in part to the carbonyl group. An unidentified peak definitely appears at 13μ. The sapphire material increasingly absorbs in the region from about 8μ to 25μ, so part of the large black body curve basically on the long wavelength side is due to the infrared emission from the heated sapphire.

The carbon dioxide band is weaker in Figure 23, which could be due to additional absorption by rock salt; however, the unidentified band at 13μ is of similar intensity.

To bypass the absorption and infrared emission of the sapphire, a pellet was burned in the open, i.e., not enclosed in the sapphire-tube container. This sample burned with a flame as expected. Its emission spectrum is shown in

42
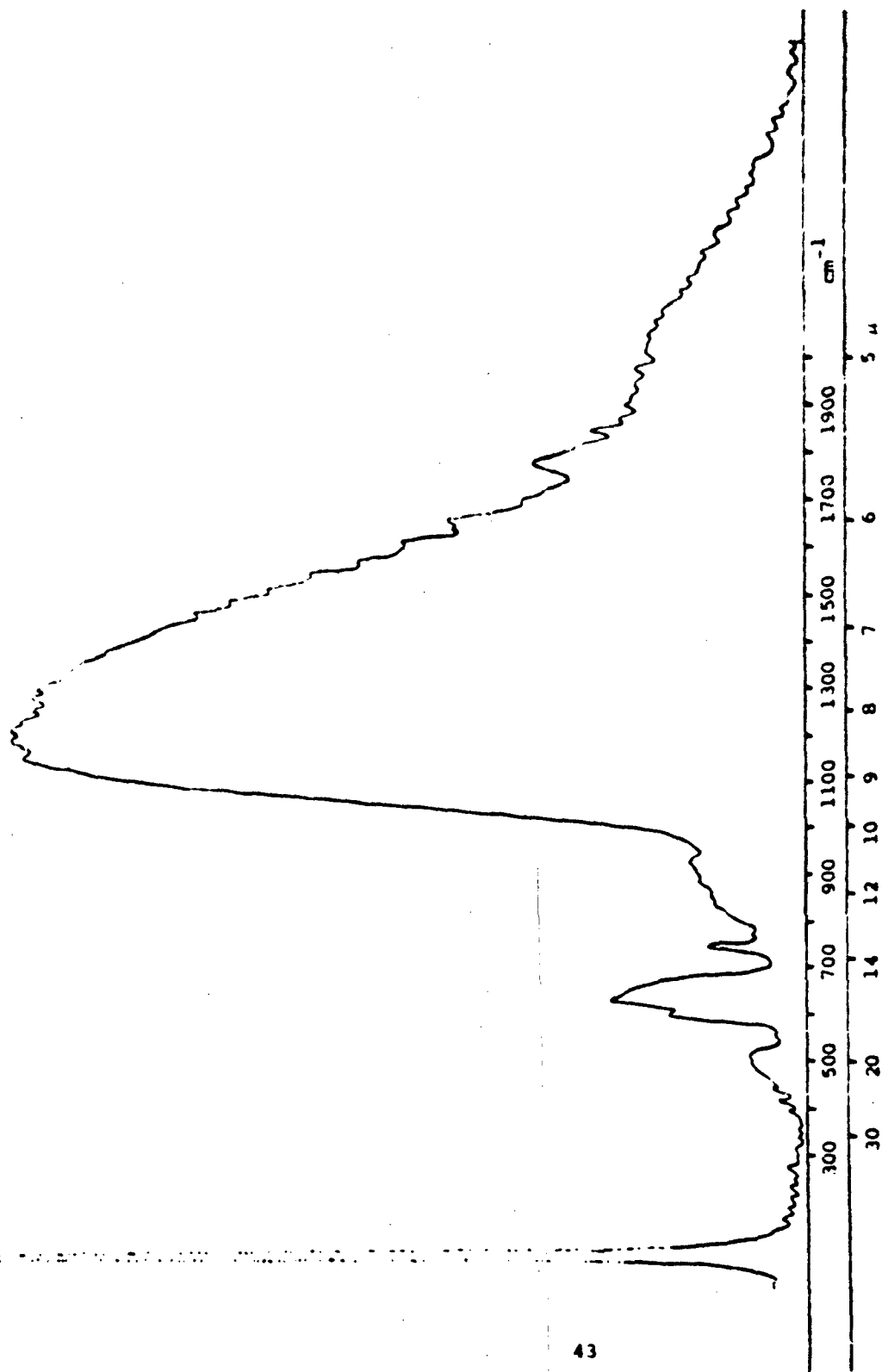
Figure 22. PYROTECHNIC ENCASEL IN SAPPHIRE TUBE-RADIATION
THROUGH ROCK SALT WINDOW

43
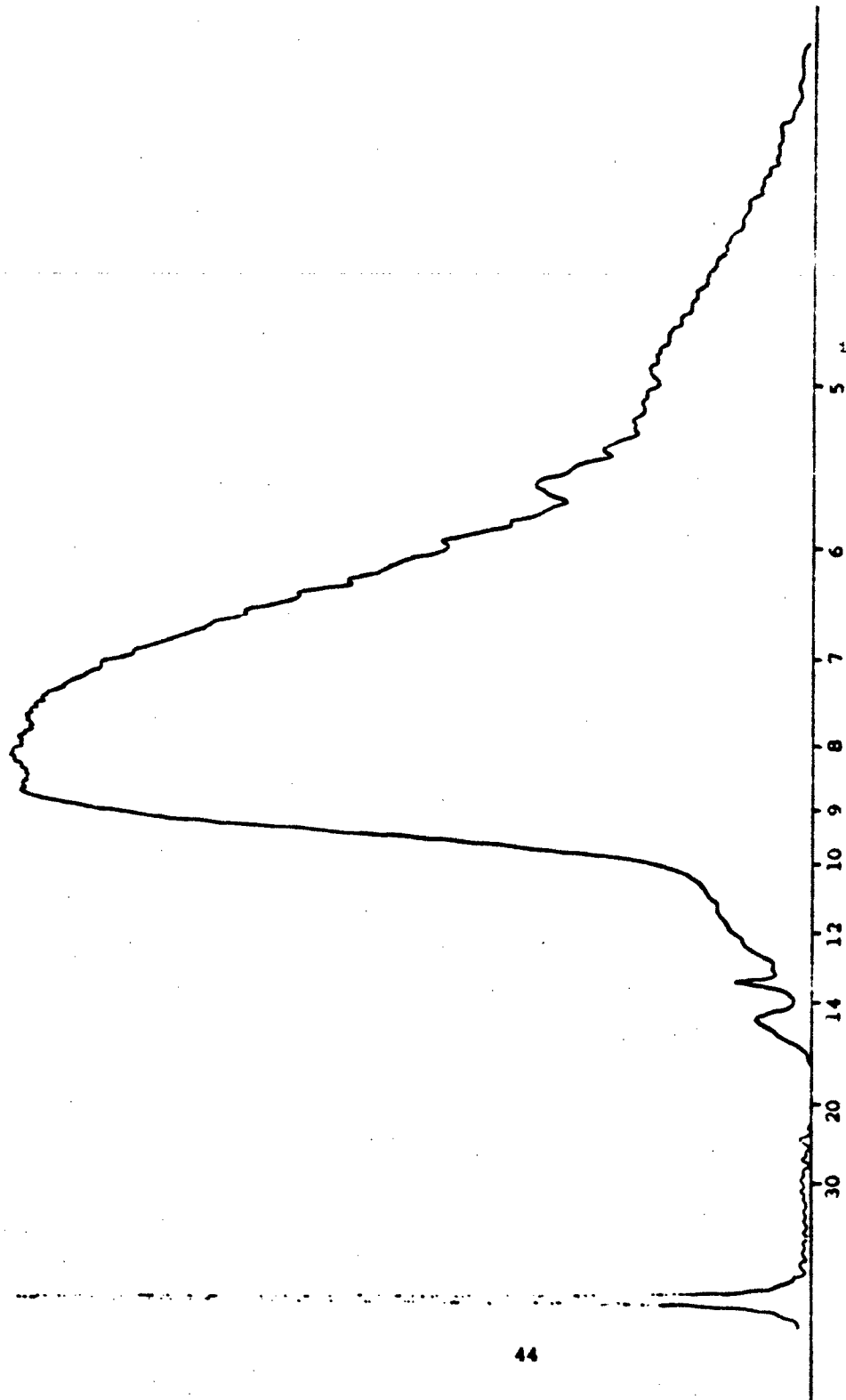
Figure 23. PYROTECHNIC ENCASED IN SAPPHIRE TUBE-RADIATION
THROUGH ROCK SALT WINDOW

44

Figure 24. The major difference is the presence of the strong CO_2 band at 4.2µ. The OH stretching band also appears at the 5.7µ position. The numerous spikes from about 14µ and longer. as well as some of the structure on the black-body curve. are thought to be due to the low frequency modulation of the flame. which appears to mask any emissions that would be due to the agent and CO_2.

Figure 25 is the result from a second pellet burned in the same way as for Figure 24. In this case, however the pellet did not burn with a flame but combusted as would be expected when encased in the container. This nonburning is indicated in Figure 25, which shows the absence of the low frequency modulation produced by the flame. The bands at approximately 5.7µ. 6.0µ, and 13µ reappear. The weak band at 14µ to 15µ is thought to be part of the CO_2 band.

Figure 26 is the emission spectra of a hot soldering iron. A pellet was combusted so the glove box was filled with the white CS smoke, then the radiation from the hot soldering iron was again impinged on the interferometer sensor, Figure 27. The two curves are essentially the same indicating no energy absorption, which further indicates that the agent is in a finely divided colloidal suspension; i.e., cool smoke. A comparison of these two curves. Figure 26 and 27, with Figure 23. indicates the emission spectra of the flare and the soldering iron are similar with minor exceptions. These exceptions would correspond to slightly higher intensity of the CO_2 band at 4.2µ and 15µ, respectively, and slightly higher intensity due to H_2O vapor. Thus, on the basis of these results, the absence of a spectrum of the CS agent is noteworthy and the emission spectrum is due to the chemical reaction.

The work with the interferometer was brief and only exploratory, so a complete series of systematic experiments could not be carried out and the interferograms were not of sufficient quality to attempt a more detailed analysis. Some species appeared consistently and some anomalies occurred, such as CO_2 at 4.2µ in one figure, but not in another. These experiments, however, indicate the potential of this type of instrumentation for study on this program.

IX. MASS SPECTROMETRY STUDIES

The Bendix Time-of-Flight mass spectrometer was used as an analytical tool to detect any differences in the upper,
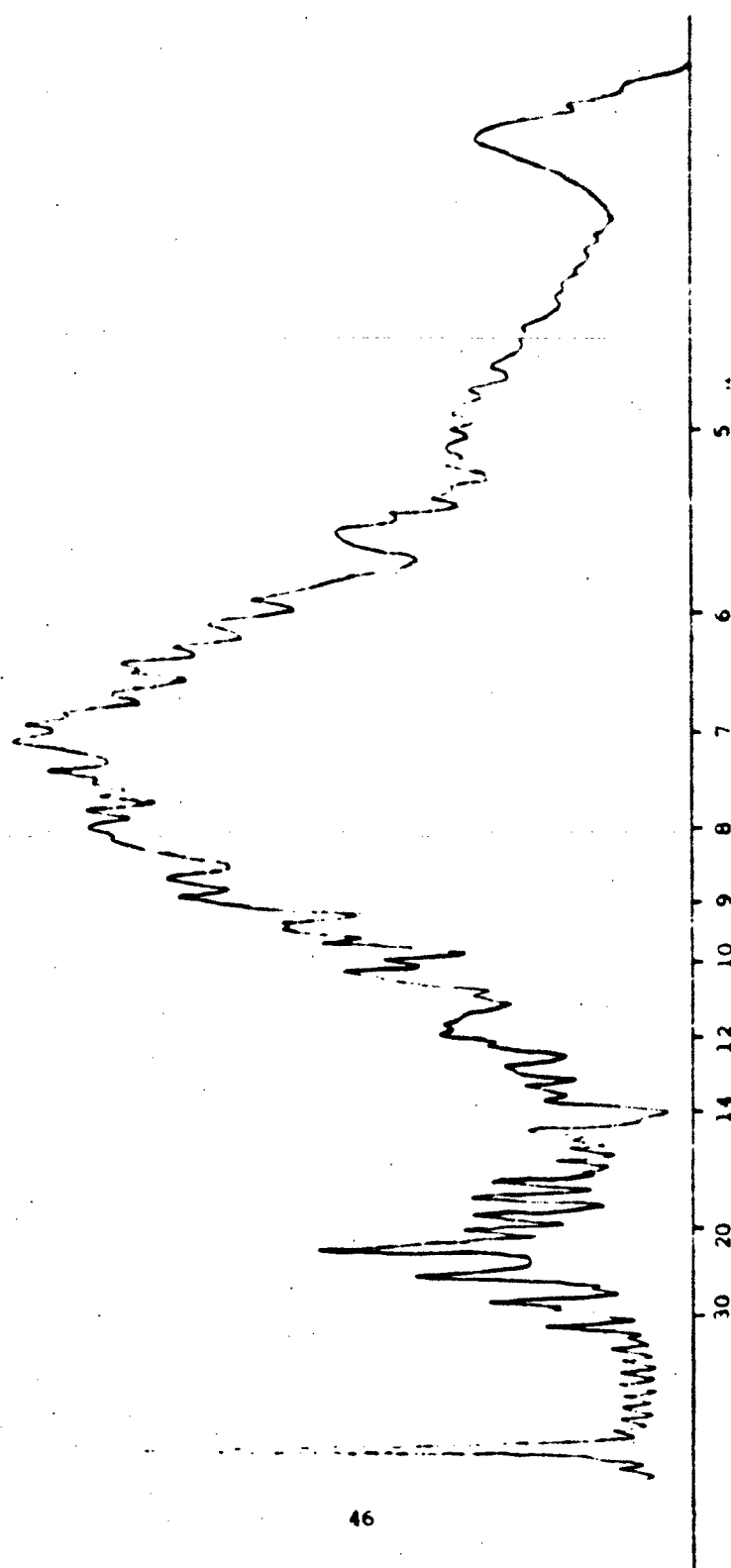
Figure 24. PYROTECHNIC BURN-ROCK SALT WINDOW ONLY

46
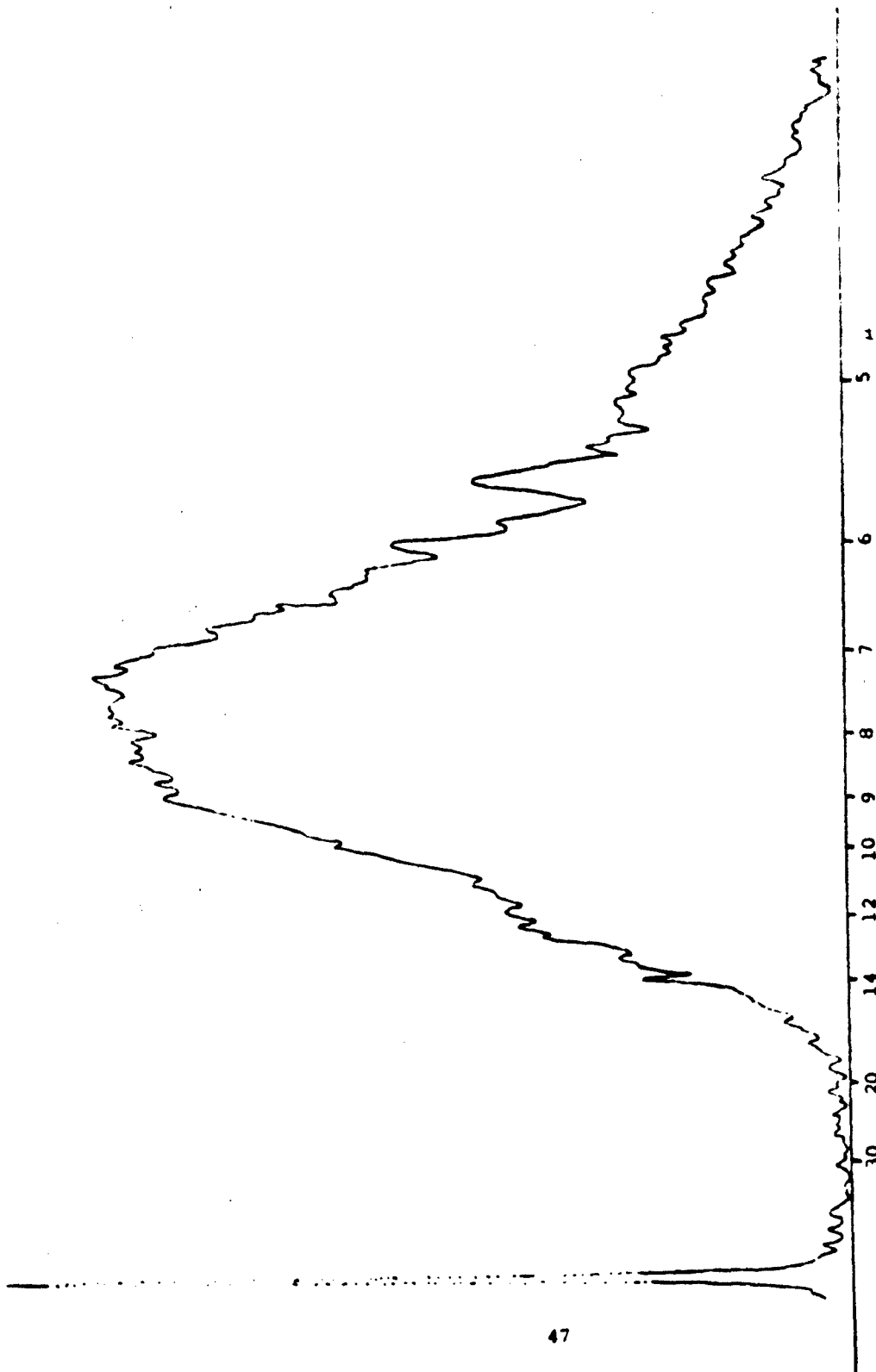
Figure 25. PYROTECHNIC RADIATION-ROCK SALT WINDOW (9 sec.)

47
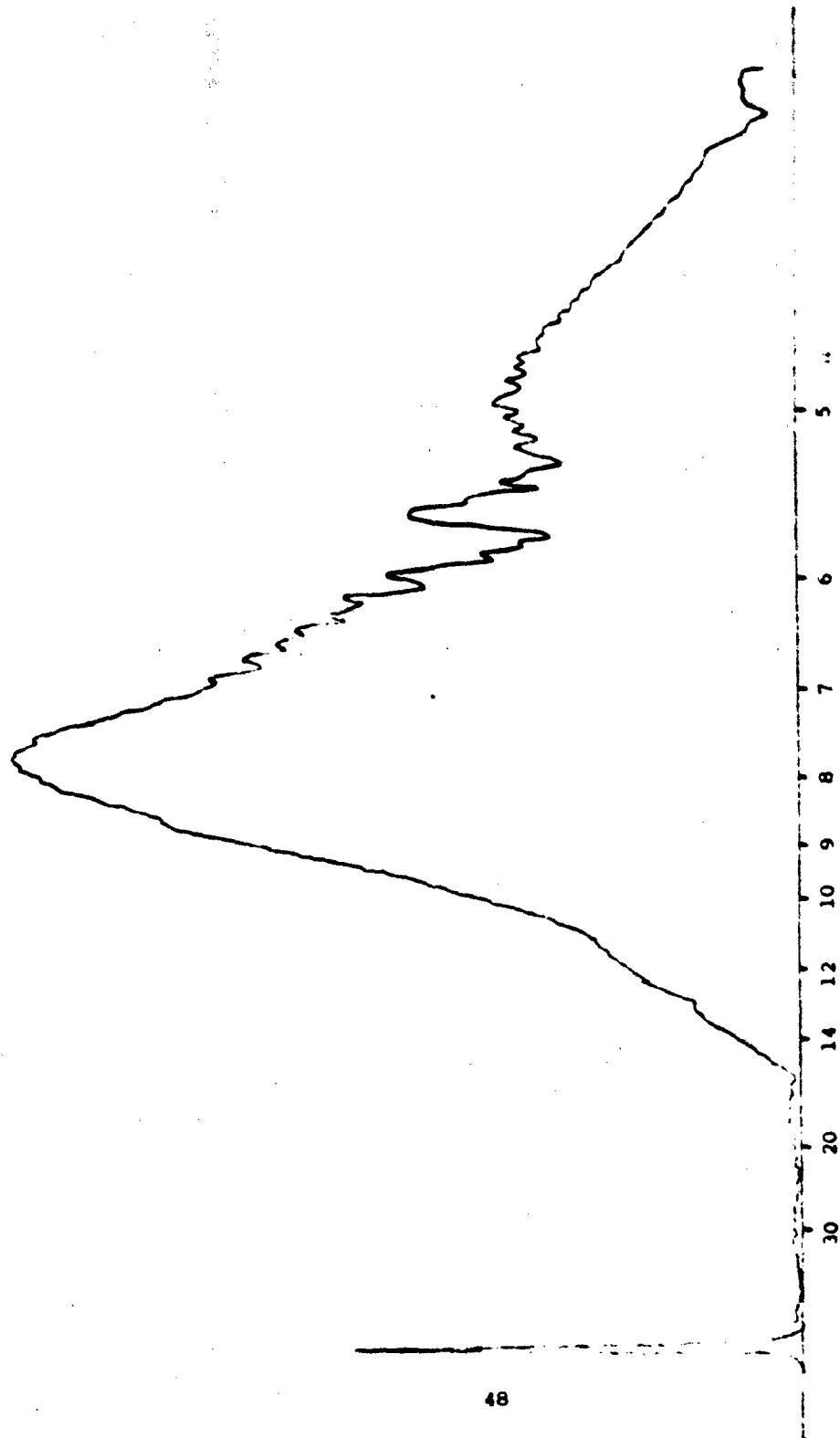
Figure 26. EMISSION FROM SOLDERING IRON-ROCK SALT WINDOW

48
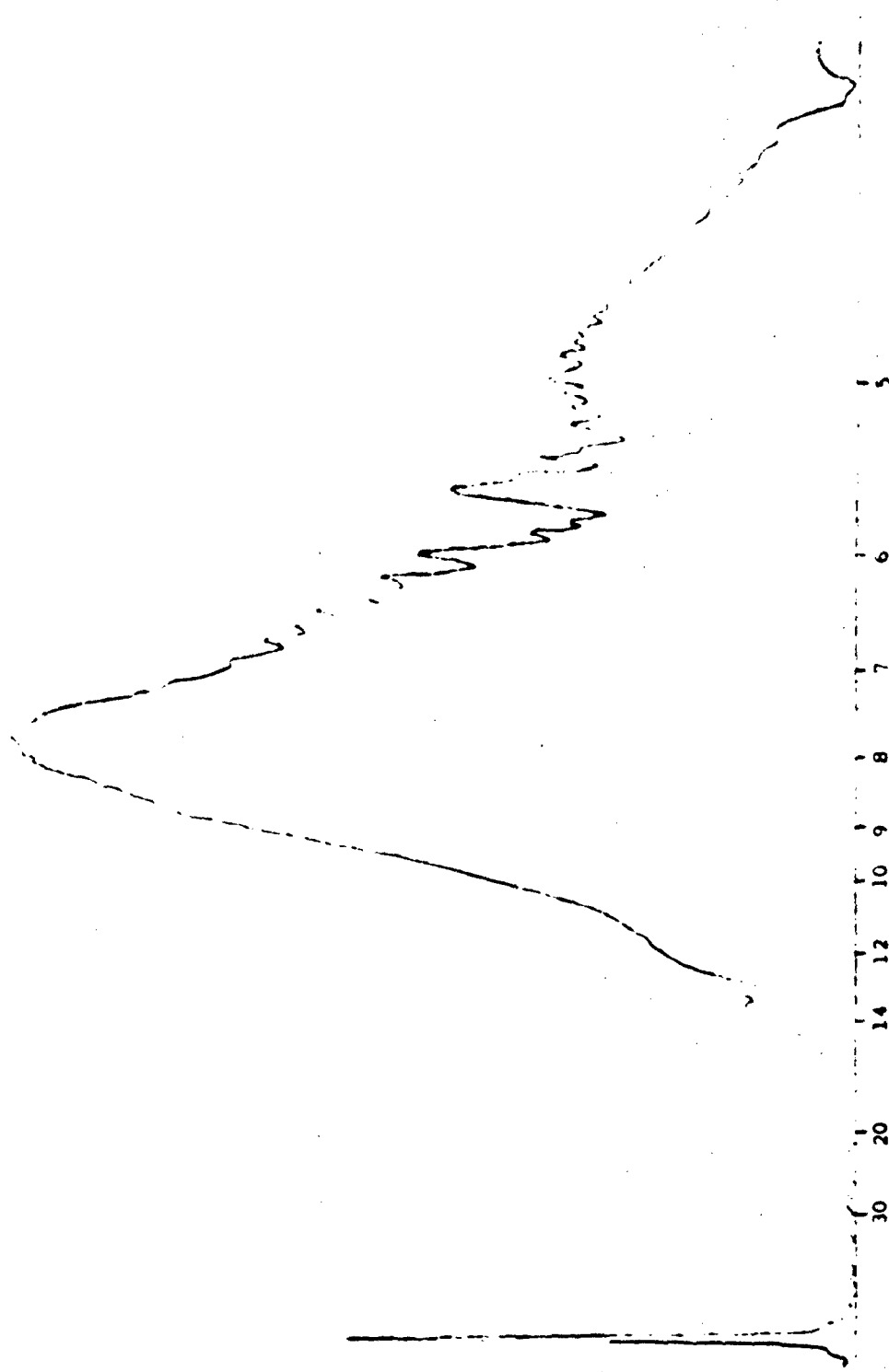
Figure 27. SOLDERING IRON EMISSION THROUGH PYROTECHNIC SMOKE-ROCK SALT WINDOW

49

center, and lower portions of the molten zone This mass spectrometer is sufficiently fast to detect differences in the composition as the zone passed by a probe, if such a sample could be collected and not overload the instrument. To handle this problem three small samples adjacent to each other were collected simultaneously for analyses in the mass spectrometer. This technique would not detect any unstable radicals but would collect any new products that resulted from degradation of the agent and the reaction products. These samples were then passed into the mass spectrometer.

A pyrotechnic containing CS enclosed in a quartz tube was fitted with three No. 23 gauge capillary tubes super-imposed as shown in Figure 28. These tubes were connected through three valves to separate small evacuated glass collecting chambers. A gear train was used to ensure that the valves would operate simultaneously. A schematic diagram of the overall device is shown in Figure 29. When the vertical travel of the combustion zone was in line with the three capillaries, the valve train was opened momentarily to collect samples from the zone. Initially the probes were 0.019-in. outside diameter and 0.036 in. apart. After a preliminary analyses these were considered too large and far apart. The second group were 28 gauge, 0.014-in. diameter. Both of these tests were not complete because of a cracked tube. The third set from which the data was obtained were 23 gauge needles that represented a total height of 0.075 in.; i.e., about two-thirds of the thickness of the molten zone.

The samples collected in the evacuated cells were sub-sequently connected to the mass spectrometer for analysis.

The samples used in these studies were

  1. CS agent only,

  2. composition of combusting pyrotechnic at the molten zone, and

  3. three segments of a combusting pyrotechnic that had been quenched with liquid nitrogen.

The samples taken from the combusting pyrotechnic were then simultaneously cooled with liquid N_2 and pumped down to a high vacuum ($\sim$5 x 10^{-6} Torr). This was done to remove the preponderance of low mass species, which, because of their higher concentrations and higher vapor pressures, were satur-ating the detector in the mass spectrometer and "drowning out"

Figure 28. SCHEMATIC DIAGRAM OF PROBE

23-Gauge
Stainless
Tubes

PYROTECHNIC

QUARTZ SLEEVE
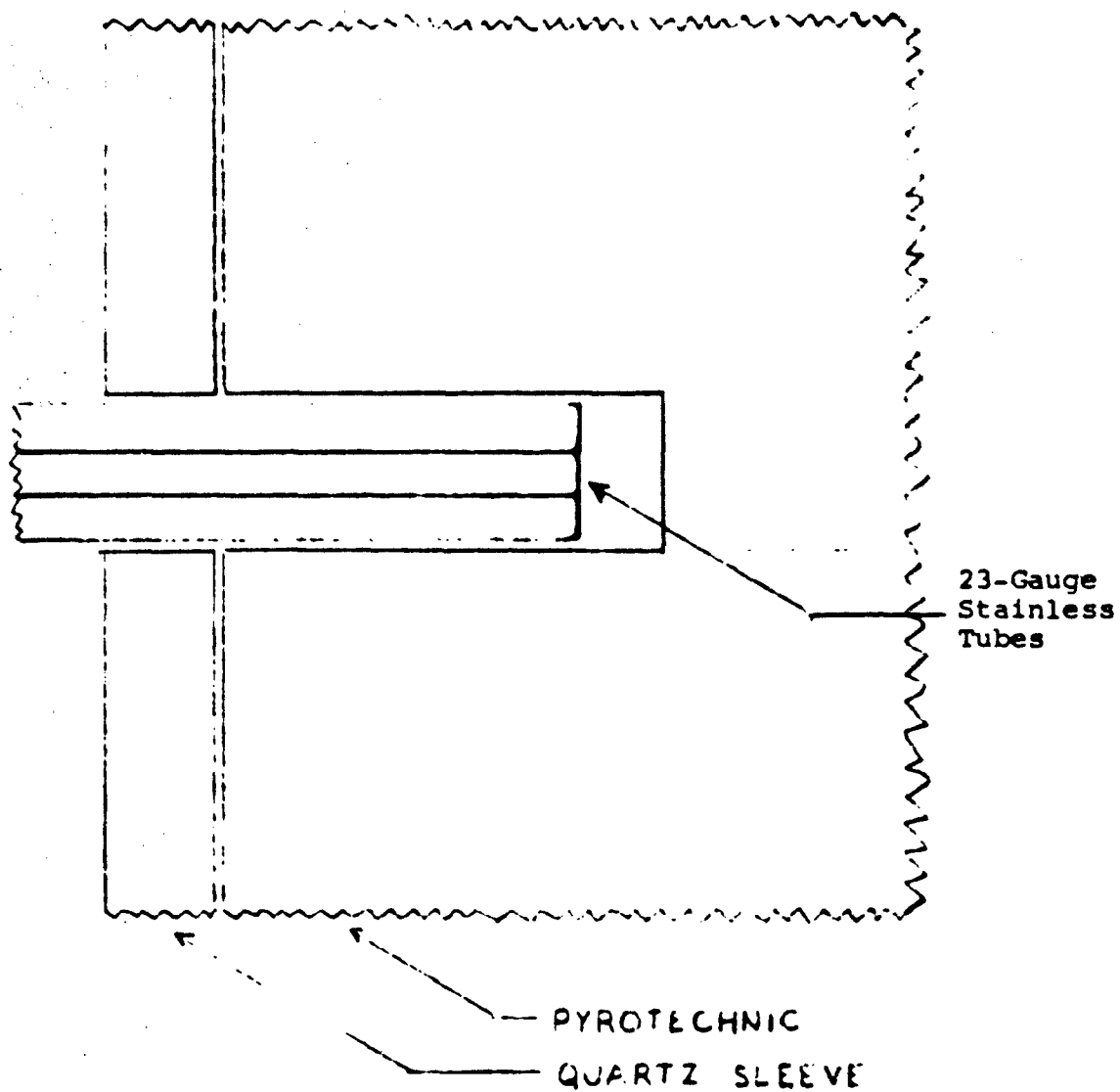
OVERALL HEIGHT OF PROBE STACK: 0.0750 in.
CENTER TO CENTER DISTANCES   : 0.0125 in.

51
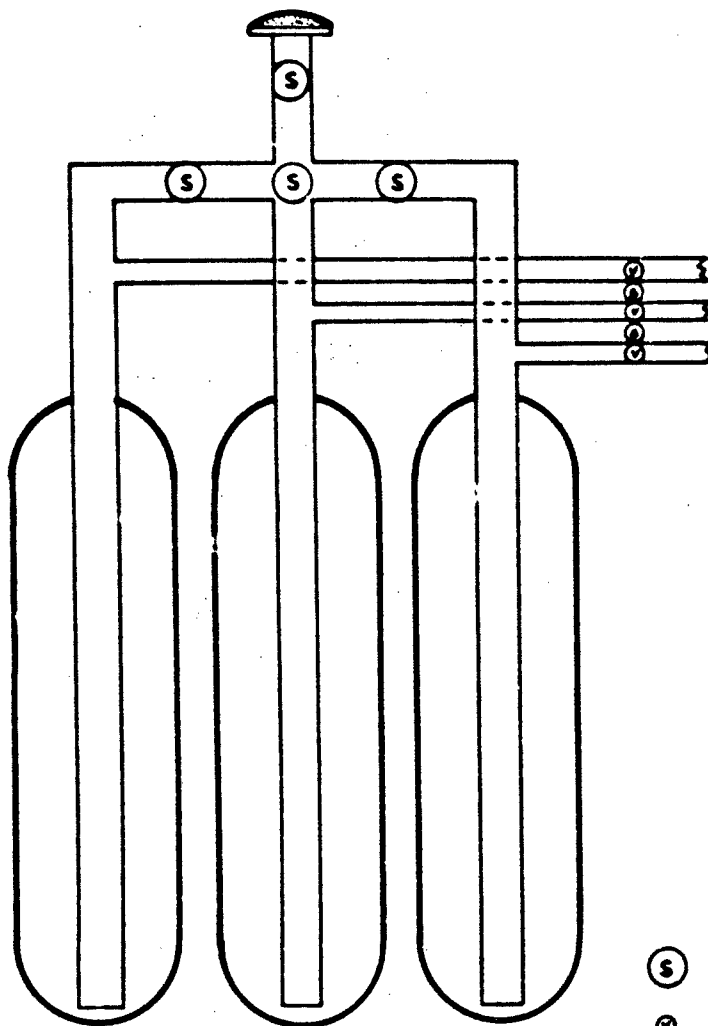
TO PROBES
SEE FIG. 2❸

Ⓢ   VACUUM STOPCOCK

Ⓥ   NUPRO VALVE. SERIES 8W
    316 SS. GEARED STEM

☉   GEAR

Figure 29.   MASS SPECTROMETER SAMPLING DEVICE

the higher mass species. These higher mass species were
resolved when the samples were rerun following the liquid
N_2 trapping.

The composite of these samples are summarized in
Figure 30. Definite differences can be seen in the pattern
for pure CS and the samples collected in the middle and
bottom probe.

It was again found that the top probe chamber had
developed a crack and lost the sample. The results of
Figure 30, as well as the melt zone of a quenched sample is
summarized in Table 3. The first column lists the mass num-
bers, the second the relative intensities of the background
of the instrument, based on the intensity of the N_2 or CO_2
line as a standard for comparison. The next three columns
give the relative intensities of the melt zone. These
assignments are to be considered tentative, since calibration
curves were not prepared and, therefore, comparisons of the
various columns should be made with this limitation in mind.
Thus, keeping this restriction in mind, the comparison of all
four columns indicates that the three samples, melt zone,
middle, and bottom probes show nearly the same mass fragments
for the range of mass number 12 to 45. and that of CS shows
mass fragments similar to the background in this range. For
the mass range from 45 to 100, the bottom probe shows lower
intensities than the middle probe, and both columns are
lower in intensity compared to pure CS and the melt zone.
The melt zone and CS show, however, approximately the same
intensities. From the mass range, from 100 and greater,
this comparison of the middle and bottom probes, respectively,
was not possible. The comparison of CS and the melt zone
indicates, however, that the intensities are approximately
the same. Attempts were made to make certain the assign-
ments of masses proposed in the table.

For this purpose the mass spectrograms of 1) perfluoro-
kerosene, 2) unreacted pyrotechnic, 3) melt zone, and 4) ash
were prepared and are illustrated in Figure 31. This was
done to establish the mass numbers with a greater degree of
accuracy. Although the standard sample was a great help,
varying pressures in the ion source would not allow simple
juxtaposition of the standard and unknown spectra for direct
comparison. The separation between peaks per mass number is
greater in 1), the last peaks being mass 100, 119, 131, re-
spectively. The last three peaks in 3) and 4) correspond to
mass 120. No significant masses of this weight range are
apparent in 2), the unreacted material.

Figure 30. COMPOSITE OF MASS SPECTRA

TOP PROBE

MIDDLE PROBE

BOTTOM PROBE

PURE CS

Table 3

RELATIVE INTENSITIES OF OBSERVED MASSES

Mass No.	Back-ground	Pure CS	Melt Zone	Middle Probe	Bottom Probe	
				Relative Intensities		
12	5		6	16	12	C
13			2	2	2	CH
14	37	36	68	45	78	N, CH_2
15	5	12	27	29	12	CH_3
16	12	30	90	78	100	O_2
17	8	100	100^+	100^+	100^+	NH_3
18	40	100^+	100^{++}	100^{++}	100^{++}	H_2O
19			40	23	20	
20			16	10	8	
21						
22				2	4	
23						
24				7	2	

Table 3 (cont.)

Mass No.	Background	Pure CS	Melt Zone	Middle Probe	Bottom Probe	
			Relative Intensities			
25			16	24	8	
26	4	16	99	100	14	CN^+
27	28	34	100^+	100^+	44	HCN
28	100^{++}	100^{++}	100^{++}	100^{++}	100^{++}	N_2 or CO
29	55	40	100^+	100^+	100	CH_3-CH_2
30	7	8	76	100	60	
31	4	4	100^+	88	36	
32	100^+	100^+	100^+	100^+	100^+	O_2
33	3	2	10	4	16	
34	3	4	7	4	10	
35		5	11	4	2	Cl
36	3	10	20	10	10	HCl
37		14	53	14	8	
38		30	100	22	14	CCN

Table 3 (cont.)

Mass No.	Background	Pure CS	Relative Intensities Melt Zone	Middle Probe	Bottom Probe	
39	7	50	100+	100	42	K
40	25	30	50	55	74	
41	24	25	30	100+	90	
42	6	16	30	93	38	
43	20	100	76	100+	98	
44	105	34	100+	100+	100+	CH_3 $C\!\!\stackrel{H}{=}\!\!O$
45		10	100+	28	38	
46		2	100	8	16	
47		3	12	6	6	
48		2	7	5	2	
49		20	44	6	2	
50		100+	100+	14	6	C=C-CN
51		100+	100+	20	8	H C=C-CN ClO

Table 3 (cont.)

Mass No.	Back-ground	Pure CS	Melt Zone	Middle Probe	Bottom Probe
52		45	74	10	2
53	7	10	16	22	8
54	5	6	7	14	6
55	10	22	18	100	38
56		12	10	98	36
57		32	20	100^+	74
58		28	28...	34	20
59		5	2	12	7
60		10	15	10	2
61		38	62	2	2
62		78	100	2	2
63		95	100^+	9	4
64		37	46	2	2
65		14	18	8	10

Relative Intensities

Table 3 (cont.)

Mass No.	Background	Pure CS	Melt Zone	Middle Probe	Bottom Probe
66	14	12	6	2	
67	12	12	11	7	ClO_2
68	8	12	9	3	
69	12	12	32	12	
70	6	8	70	14	Cl_2
71	12	6	23	15	
72	12	19	38	20	
73	40	63	8	2	
74	78	100			
75	100[+]	100[+]			
76	100	100[+]			
77	48	80			HC≡C⌐CN
	12	16	10		⌐CN
	8	5			

Relative Intensities

61
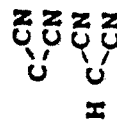
Table 3 (cont.)

Mass No.	Back-ground	Relative Intensities			
		Pure CS	Melt Zone	Middle Probe	Bottom Probe
80		12	16		
81				8	7
82				8	
83		8		34	12
84		18	28	18	
85		22	33	12	13
86		26	38		Cl_2O
87		32	49		
88		24	37		
89		18	37		
90					
91				6	20
92				12	20
93		18	24	12	23

Table 3 (cont.)

Mass No.	Background		Pr: CS	Melt Zone	Middle Probe	Bottom Probe
		Relative Intensities				
94	6					
95						
96						
97						
98						
99						
~100			8; Hg	95 Hg	12 Hg	30 Hg
~108			10 (wide group)	20 (wide group)		C_6H_5Cl (112)
~120					24	
~122			65 (wide group)	88 (wide group)		
~138			32 (2 peaks)	43 (2 peaks)		(structure) 136

Structure (Bottom Probe, 136): cyclohexane ring substituted with Cl and $C=CH$ (vinyl, H H).

63

Table 3 (cont.)

		Relative Intensities			
Mass No.	Back-ground	Pure CS	Melt Zone	Middle Probe	Bottom Probe
~145		100	100$^+$ (wide peak)		<chemical structure: cyclohexene ring with + charge, C=C–CN and CN groups> 136
~155		34/16 (2 peaks)	42 (wide peak)		<chemical structure: cyclohexane ring with Cl, H, C=C–CN, CN, H groups> 162
~167		22	20		<chemical structure: cyclohexane ring with Cl, C=C–CN, CN, H groups>
~180		100$^+$/60 (2 peaks)	100^{++} (wide peak)		
~200		50 Hg (wide group)	16 Hg (wide group)	30 Hg	36 Hg

64
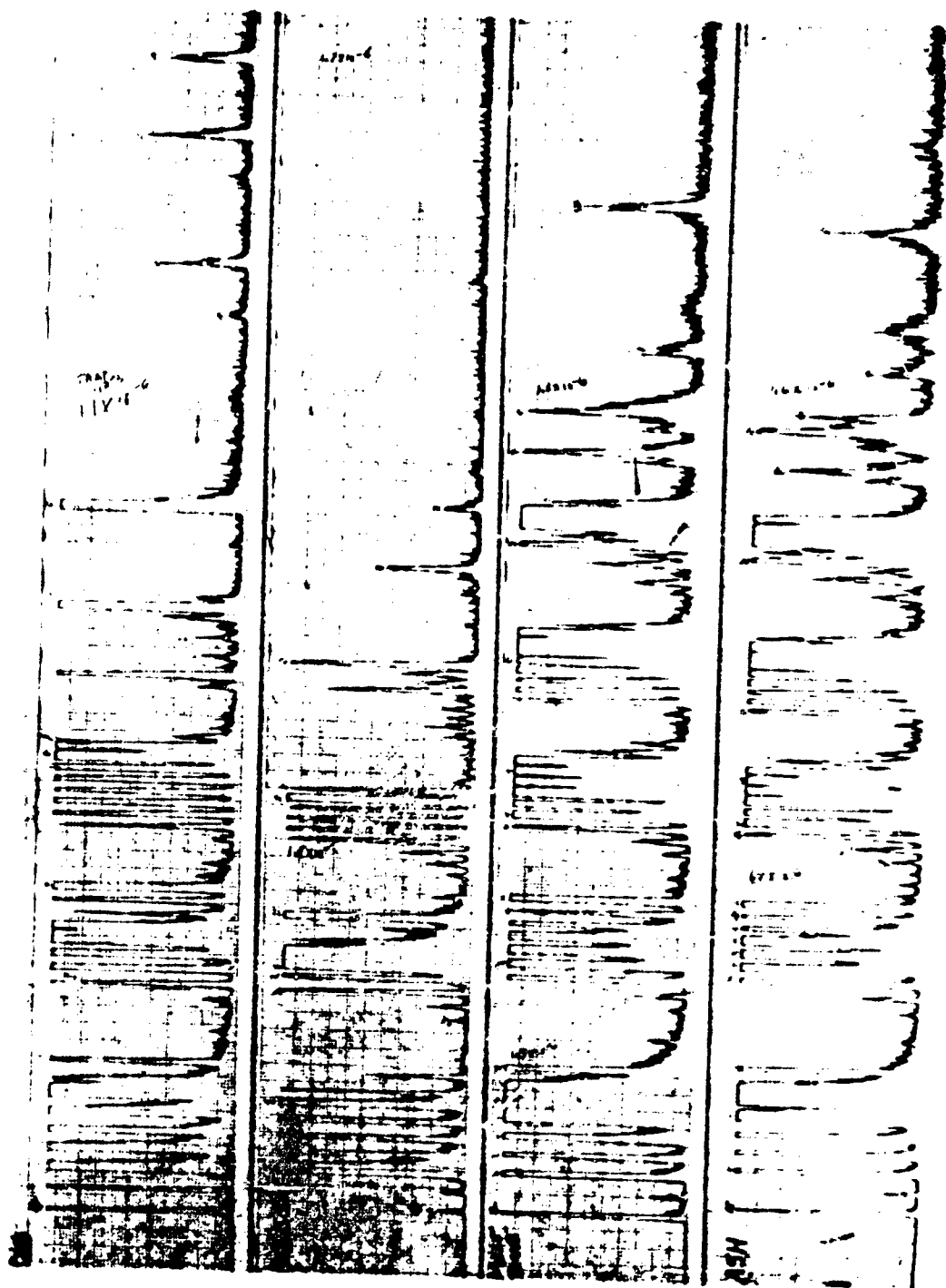
Figure 31

MASS SPECTRUM RESULTS

The spectra of 3), the melt zone, and 4), the ash, are identical. The differences between these spectra and that of 1), the unreacted material, are recorded in Table 4.

It should be emphasized that these results are of first attempts, and that employment of internal standards, and more refined sampling techniques for the ion source would result in more detailed and more accurate data.

X. SUMMARY

A number of physical techniques were used to study reaction products, temperature and rates of combustion of a pyrotechnic mixture containing the agent, CS, and the simulant, 1-methylaminoanthraquinone. These included emission spectroscopy, rapid-scan spectrometry, infrared absorption spectrometry, interferometry, mass spectrometry, color and infrared cine spectroscopic and thermocouple temperature measurements. The study was essentially exploratory so time did not permit the refinement of some promising experiments. Interferometry and mass spectrometry offer the most promising techniques for a more detailed study of the reaction zone.

Chemical purity and powder or crystal size and pressure used to form the pellet, as well as the agent influences the combustion rate and temperature. The initial infrared absorption studies of the hot gases from the orifice indicate it to be combustion products from sugar and the agent. Agent was found trapped in the remaining char.

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Table 4

MASS SPECTRUM RESULTS

Mass No.	Ash and Melt Zone	Intensities Unreacted	Probable Species
12	16	2	C
13	2	2	CH
14	50	68	N, CH_2
15	52	48	CH_3
16	58	48	O_2
17	69	56	NH_3
18	72	64	H_2O
19	27	16	
20	42	6	
21			
22			
23			
24			
25	1	3	
26	16	4	CN^+
27	48	36	HCN
28	64	76	N_2 or CO
29	66	60	CH_3-CH_2
30	64	12	
31	26	6	

Table 4 (cont.)

Mass No.	Ash and Melt Zone	Intensities Unreacted	Probable Species
32	22	63	O_2
33	56		
34	2		
35	2		Cl
36	1	2	HCl
37	2	3	
38	5	4	CCN
39	16	15	K
40	61	22	
41	51	20	
42	64	12	
43	60	56	
44	61		CO_2 $CH_3C{\overset{H}{\underset{O}{\diagdown}}}$
45	54		
46	2		
47			
48			
49			
50	2	2	C=CCN
51	18	3	HC=CCN ClO
52	28	2	

Table 4 (cont.)

Mass No.	Ash and Melt Zone	Intensities Unreacted	Probable Species
53	20	2	
54	50	2	
55	42	10	
56	61	4	
57	50	5	
58	56	18	
59	12		
60	2		
61			
62			
63	2		
64	8		$C{<}_{CN}^{CN}$
65			
66	8		
67	4		ClO_2
68	23		
69	12	6	
70	32		Cl_2
71	58		
72	28		
73	31		

Table 4 (cont.)

Mass No.	Ash and Melt Zone	Intensities Unreacted	Probable Species
74			
75			
76		2	
77			
78	4		
79	10		
80	4		
81			
82			
83	4		
84	18		
85	5		
86	9		Cl_2O
87			
88			
89			
90			
120	8		

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Chemical agent dissemination	

13. ABSTRACT A number of physical techniques were used to study the reaction products, temperature and rates of combustion of a pyrotechnic mixture containing the agent CS or the simulant 1-methylaminoanthraquinone. These included emission spectroscopy, rapid-scan spectroscopy, infrared absorption spectrometry, interferometry, color and infrared cine studies, and spectroscopic and thermocouple temperature measurements. Spectroscopic temperature measurements were performed using the two-line, the two-color, and the maximum radiant energy wavelength techniques. The difference in these and thermocouple results can be due to the total region observed by each technique. Chemical purity, powder and/or crystal size of the constituents and pressure used to produce the pellet influenced the rate of reaction and temperature. The chemical species observed by emission infrared absorption spectrometry and interferometry were essentially those associated with the combustion of the fuel. Experiments were not sufficiently refined to identify the lesser species segments in the combustion zone, however, interferometry and mass spectrometry offer the best techniques. A study of preliminary mass spectrometry data do show some masses that could be from agent decomposition.

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14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Reaction products Temperature Ratio of combustion Emission spectroscopy Rapid-scan spectroscopy Infrared absorption Interferometry Mass spectrometry						

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